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EDITORIALS.

THE INDUSTRIAL CHEMIST AND HIS JOURNAL.

THE necessity for a journal published in the interests of the American Technical Chemist and Chemical Engineer must be apparent to all engaged in manufacturing pursuits, more especially those having to do with processes and problems of a chemical character.

Publications devoted to printing the results of chemical investigation and research are not lacking. In fact, if they were fewer and their matter edited and condensed, their readers would be the gainers. We are, however, fortunate in having them, and we must accord all credit and honor to those engaged in their publication for their self-sacrificing efforts in the interest of our beloved science, since the work of necessity must be a labor of love, as the monetary rewards are meagre if not entirely lacking, or the publications are conducted at a loss.

Let it not be said of the Technical Chemist that he loves his science any less than his brother, who devotes his time to research or teaching. The Society desires to enlist the coöperation of the Industrial Chemist in this Journal. It does not seek the publication of confidential matters, or the secret processes of any company or works, but it believes that a certain liberality in publishing broader information on subjects of manufacturing interest will be beneficial. For example, witness the monumental works of Lunge. These pages will be open for the publication and discussion of topics, the reading of which will materially increase the reader's knowledge of not alone that branch of chemistry in which he is working, but of its whole industrial field, and he will obtain many hints of value.

To illustrate—observing the reaction taking place in the metallurgy of lead, wherein its sulphide reacts on its sulphate when heated, producing metallic lead and sulphurous anhydride, a like reaction was suggested in the case of similar barium compounds, hence an ingenious and cheap process for barium hydroxide was devised and patented. By applying a modification of J. Lawrence Smith's method for the determination of alkalis in silicates, using calcium chloride and limestone, a good method was devised in the laboratory of a works the writer was connected with, for the extraction of potash salts from feldspar. Should our supplies of these salts from Germany be curtailed, or stopped, by reason of war or tariff conditions, the process would be economically practicable. This was hinted at in a paper read by Cushman before the New York Section last winter.

We still seek a practical process for the utilization of the chlorine in the ammonia soda process, although Tucker has shown how the alkaline chlorates can be manufactured from calcium chloride by electrolysis and double decomposition.

The recovery of zinc associated with pyrite has been and is engaging the attention of the chemist, and

it looks as though it would be solved by an electrical process. Fusel oil is scarce and high. If the proper ferment or yeast can be propagated, amylic alcohol could be manufactured cheaply and profitably.

We could continue on in this suggestive way, but enough has been written to show the value of putting before our readers subjects which not alone may interest them but the entire chemical world.

The chemical engineer is called on in our industry to adapt the material best suited to the process in hand. In the laboratory this may be glass, porcelain, platinum, or what-not; but from their expense or fragile character, these are not usually permissable in large scale operations. He has, therefore, to use the construction material at command, as say iron, lead, copper, alloys and brick. To do this properly he must have, not alone the training of a chemist but also that of an engineer, and should have at hand the most recent developments of the science which pertain to the installation or improvement of existing processes.

We often hear of the success of a laboratory method, and its failure when applied on a manufacturing scale. In many cases failure is due to lack of engineering knowledge, or of natural laws governing the changed conditions. We read in the last report of Admiral N. E. Mason, Chief of Bureau of Ordinance, U. S. Navy, that experiments in drying nitrocellulose by means of alcohol met with success in the laboratory, but were unsuccessful on a working scale, for reasons that to him remain obscure. We would like to know the reason why; probably the chemical engineer can tell us.

T. J. PARKER.

THE ETHICS OF ENGINEERING SUPPLIES

THE crusade, which during the last few years has been carried on in the magazines against the so-called patent medicines and other articles of this nature, has produced a great and lasting good. The agitation which culminated in the national Food and Drugs Act of 1907 also has served to awaken the public to the many deceptions which are being practiced and the many worthless preparations for general domestic use which are on the market. The result of this movement has been first to force a great many of the more palpable frauds to be withdrawn from the market, and second to provide for the correct labeling of all others, so that the purchasers may be in position to buy intelligently.

Only those materials, however, which may be classified under the head of food and drugs for the human system come within the scope of this legislation. A steam power plant considered as an organism has also afflictions for the cure of which many so-called patent or secret medicines are offered for sale. The average engineer is no more in position to judge of these preparations than is the housewife able to distinguish between a valuable or a worthless proprietary medicine. Such imposition is found in many of the water softeners and boiler compounds which are offered for sale as panaceas for all the ills to which the steam boiler is subject. Not infrequently the value of such materials varies inversely as their cost. Our attention has recently been called to a certain widely advertised "alloy" guaranteed to prevent the corrosion or pitting of boilers, and which was sold at an exorbitant price. It proved to be ordinary feathered zinc. Many boiler compounds are mixtures of soda ash, and almost any usually worthless filling material that may be at hand when the material was put together.

A campaign of education might well be undertaken which would serve to place before the consuming public the danger in promiscuously buying, and ignorantly using, any mixture which a smooth-tongued salesman may see fit to offer. It may be argued that since we have in our community a large number of skilled commercial analysts, there is no adequate excuse for promiscuous buying, but this does not entirely relieve the situation. So long as goods intended for the engineering public are made and vended by salesman and circular without restraint or control they will be sold, even though improperly labeled or actually fraudulent. The list of products used by engineers and peculiarly susceptible to admixture is large: pigments, oils, varnishes, solvents, boiler compounds, lubricating oils, metals and alloys are a few of them. The list of products capable of being sold by means of unwarranted statements in regard to useful qualities or properties is also large. The chemical fake assumes many guises. The consideration of general ways and means, educational and legislative, for eliminating it is worthy the consideration of all chemists interested in the upbuilding of the profession and extending its usefulness.

WILLIAM H. WALKER.

THE SUGAR INDUSTRY IN ITS RELATIONS TO THE UNITED STATES.

The per capita consumption of sugar in the United States was 77.54 lbs. in 1907, which exceeds that of any previous year.

	1907.	1906.
The total consumption was, in long tons	2,993,979	2,864,013
consisting of Domestic cane (La. & Texas)	264,968	267,947
Domestic beet	375,410	300,317
Maple	10,000	6,000
Molasses sugar	6,249	8,150
Total domestic	656,627	582,414
Hawaii (all cane)	418,102	343,857
Porto Rico (all cane)	212,853	193,978
Philippine Islands (all cane)	10,700	41,900
Cuba (all cane)	1,340,400	1,165,994
Total receiving tariff concession	1,982,055	1,745,729
Foreign raw cane	347,509	357,057
Foreign raw beet	6,780	175,827
Foreign refined beet	949	2,734
Foreign refined cane	59	252
Total Foreign paying full duty	355,297	535,870

The refining of this sugar was accomplished as follows:

	1907.	1906.
By sugar refineries	2,465,888	1,440,334
By beet sugar factories	375,358	300,059
By Hawaiian cane	1,674	16,964
By Foreign refineries	1,008	2,986
Total amount refined sugar	2,843,928	2,760,343

From the above, it may easily be seen that this country is one of the largest sugar consumers of the world, but that although our domestic beet sugar industry is advancing (mainly in the West) we are still in no position to compete with the raw cane sugar production of more tropical countries.

In the countries producing this raw sugar, the processes of manufacture have received close scientific study, resulting in a high development of technique. A generation ago beet sugar manufacture advanced more rapidly than cane, but the last few years have brought cane sugar manufacture also up to a high degree of efficiency and economy. Not only have some new varieties of cane of superior character been developed, but better modes of cultivation have been worked out. Greatly increased yields of sugar from the cane have been obtained through increasing the extraction of juice from cane by employing preliminary crusher or shredder and pressing three or even four times instead of only twice as formerly in three-roller mills. Macerating with abundant water aids in this added extraction, which now rises to 90 or 95 per cent. of the sugar in the cane as contrasted with 75 or 80 formerly obtained. Some factories employ as much as 30 or even 40 per cent. of the weight of the cane in water of maceration, applying it in multiple, instead of all at one place. Every 4 per cent. of water is thus found to increase by about 1 per cent. the extraction of sugar in cane. Better means of defecation have been developed, as in the pre-heating and super-heating devices of Deming. Hatton's new continuous defecation system promises considerable advantage, and may eliminate a great part of the filter press work. Multiple effect evaporators have reached a high efficiency, the quadruple effect being in common use. In the Lillie apparatus a reversal of both juice and steam is possible, greatly diminishing the amount of incrustation. Kestner has developed a vertical design containing tubes 25 or 30 feet long, for evaporating solutions which tend to foam, and these have been found very good for alkaline vinasse, especially as the parts can all be made of iron, keeping down the cost of construction. Much more thorough crystallization of sugar from magmas is now effected by keeping the magmas in gentle motion and lubricating the stiffening mass by occasional injections of exhausted molasses.

In raw beet sugar manufacture, as in cane sugar making, the recent advances have been made in improving the efficiency of a host of operations, rather than in developing any radically new basic principles. Recent years have seen a considerable reduction in the amount of lime used in defecating the raw juice and a satisfactory development of the Steffens process of precipitating the sucrose as a lime saccharate from the residual molasses. A pretty satisfactory outlet for the beet pulp has been found in the form of cattle food, made either by drying in specially designed kilns, or by moistening with waste molasses and feeding direct. Formaldehyde has come to play an important part in preserving sugar solutions that have to be held over during shut-downs, in lieu of lime.

The refining industry has already been so highly developed that great innovations in the technique are rare. Theoretical advance has been constant and many improvements appear in matters of detail. The system of crystallization in motion for low products has been adapted from the raw sugar industry while the use of ultramarine and sulphur dioxide has been largely discontinued, due to the operation of the pure food law.

There are several points in the process of sugar manufacture and refining where great improvement might be afforded and which should attract

the attention of investigators. A great advance would arise from a suitable electric process which could dissociate and remove the organic impurities as well as the salts from low-grade sugar solutions. A cheap substitute for bone-black, of equal efficiency and durability should prove a boon. Some good method of continuous mechanical filtration of sugar solutions would be of considerable value, and the same is true of a continuous system of purging the sugar grains from their enclosing mother-liquor after boiling. W. D. HORNE.

THE FIXATION OF NITROGEN.

HARDLY any achievement in Industrial Chemistry has attracted such wide-spread interest as have the processes which render it possible to make use of the nitrogen of the atmosphere in a commercial way. When Priestley first demonstrated that atmospheric nitrogen could be converted into nitric acid under the influence of the electric spark, he little dreamed that his discovery would some day form the foundation of a large and profitable industry. We may be a little hasty in anticipating this last assertion, but the progress which has already been made is almost an assurance of future success. The great achievements in electrotechnics have made it possible to produce electric energy in large quantity and, in turn, make it available for converting the nitrogen of the atmosphere into valuable compounds. It has been known for some time that nitrogen and hydrogen can be united by an electric discharge, or under favorable conditions, by contact with certain substances. These facts have been utilized by many inventors, but thus far, none of the inventions along these lines have proved of much practical value. The progress, however, which has been made in other directions during the last few years in fixing atmospheric nitrogen has been remarkable, and has for the time, overshadowed other achievements in Industrial Chemistry.

The process of Frank & Caro in which the nitrogen of the air is separated and combined under certain conditions with calcium carbide to form calcium cyanamide is giving very promising results. The developments of the applications of the initial trials of this process have justified the erection of several factories in widely separated localities to test its practicability on an extensive commercial basis.

The principle involving the direct conversion of the nitrogen of the atmosphere to nitric oxide and nitric acid by aid of the electric spark is no longer confined to the class-room demonstrations. The experiments of Crookes, Lord Rayleigh, Lepel and others formed the foundation for the industrial application of the earlier discoveries. While the first industrial application of this principle by the Atmospheric Products Company under the patents of Bradley & Lovejoy at Niagara Falls did not prove successful, it stimulated further research along this line, and later developments give much more promising results. In this first attempt, it was clearly demonstrated that nitric acid could be produced on a large scale, and it only remained to cheapen the cost of production. This was accomplished in a large measure by the process of Berkeland & Eyde which was similar in the main to that of American inventors except that the efficiency of the ordinary electric arc is greatly increased by flashing in a magnetic field at a very high temperature. Instead of a multitude of thin streaks of electric light, this process provides for a large disc of flame which affects a large volume of air so that the oxidation of nitrogen is much more rapid and is accomplished with much less expenditure of energy. The experimental factory for testing this principle, erected near Nottoden, Norway, having the advantage of very cheap water power, has given such encouraging results that the production will be attempted on a larger scale. Thus we have at the present time, two processes for the utilization of atmospheric nitrogen operated under entirely different chemical principles, both of which give great promise of ultimate success. Improvements are constantly being made which increase the efficiency, and lessen the cost of production, and we can rest assured that long before we have a nitrogen famine our wants will be supplied.

The importance of these inventions and their successful applications can hardly be overestimated. The demands for nitrogenous compounds, both for industrial and agricultural purposes, are rapidly increasing year by year, while the available supplies are rapidly decreasing; it is estimated that the consumption of nitrate of soda alone amounts to over 1,700,000 tons per annum, and at this rate it is predicted that the deposits will be exhausted in less than fifty years.

While the free nitrogen forms four-fifths by volume of the atmosphere, it is not probable that the

combined forms one millionth part. Considering, therefore, this inexhaustible supply, and considering what it means to agriculture and the arts if it can be utilized, the solution of the problem of conserving the nitrogen of the air in a commercial way, will be recorded as one of the important inventions of modern times.

F. B. CARPENTER.

STANDARD METHODS OF ANALYSIS.

WE have seen with a good deal of interest, a brown-covered pamphlet of thirty-two pages, published by the United States Steel Corporation in the interests of their chemical force and entitled "The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Iron Ores."

The work of developing the methods was performed by a committee consisting of: J. M. Camp, Carnegie Steel Co.; Wm. Brady, Illinois Steel Co.; W. B. N. Hawk, National Tube Co.; A. B. Clemence, American Steel & Wire Co.; E. A. Separk, Oliver Iron Mining Co.; G. D. Chamberlain, Carnegie Steel Co.

The preface explains the purpose of the Steel Corporation and the chemists in formulating these methods. "The Chemists' Committee was appointed for the purpose of unifying the methods of sampling and analysis of the materials consumed and produced by the United States Steel Corporation, with the purpose of rendering more accurate the analytical results obtained. Owing to the difference in education or practical training of the chemists in charge of the laboratories of the Steel Corporation, wherein iron ore is analyzed, a wide divergence in the methods of analysis would be expected; by harmonizing these methods, the errors incident thereto would be minimized."

We understand the work of the committee will be continued and the methods for the analysis of other materials developed.

Contrasted with twenty or twenty-five years ago, the condition of analytical chemistry at the present time in this country, and indeed throughout the world, is such that we may face the future hopefully. Many organizations have contributed to the unification of the methods which are in constant use to-day. We need only recall the work of the various committees of the Association of Official Agricultural Chemists on fertilizer, food and fat analysis, of the Committee on Uniformity of the American Chemical Society under the able leadership of Dr. Hillebrand, and more recently of the Committees of the Society for Testing Materials to realize how great has been the advance from the chaotic condition in which the unorganized methods of analysis existed a few years ago to the fairly well organized condition in which we find them to-day.

Much work remains to be done. Among the contributing organizations which are endeavoring to place commercial analytical methods on the high plane where they belong, what one could be more useful than the large corporation which employs numbers of chemists and operates many chemical laboratories in various localities and, in fact, which finds the daily routine application of analytical methods a guide and a necessity for the control of all its manufacturing operations? The pessimist will say that already we have too many and too various organizations working on the uniformity of chemical methods, and the addition of even one more to the ranks is hardly advantageous. We feel more confident in the matter and believe that for present needs, the various organizations which have been and are working out the details of methods, are working along the right lines. For the future, when they shall have accomplished their work, the representative organization of chemists in this and in other countries must see to it that all the methods of analysis are worked into one comprehensive system, which shall not be fixed for all the time, but shall be kept alive by active committees and continuous additions and improvements as the science develops.

W. D. RICHARDSON.

ORIGINAL ARTICLES.

FREE LIME IN PORTLAND CEMENT.

By ALFRED H. WHITE.

Received October 3, 1908.

This paper describes a simple microscopic test for free lime in Portland cement and discusses the result of its application to a number of commercial cements and to others made in the laboratory.

The usual analysis of Portland cement shows lime to form over sixty per cent. of the weight of the clinker, but does not give any clue to the form in which this lime exists. It is rather generally, although by no means universally, assumed that

the lime must be in a state of combination, but the evidence for this belief is almost entirely indirect, because of the difficulty of determining directly whether the lime in cement is free or combined. The application of aqueous solutions of any sort is impracticable because of the rapid decomposition of normal cement by water with resultant formation of calcium hydroxide. Anhydrous solvents for lime have been proposed, notably glycerine and a solution of oxalic acid in absolute alcohol, but the methods are at best tedious, and if free lime is detected there is always the suspicion that it may have been due to the action of moisture in the hygroscopic reagents, rather than to actual free lime in the cement. Neither can the method be applied with certainty to commercial cements which have been exposed to the air and may be partially hydrated. A solution of phenolphthalein in a non hygroscopic solvent, preferably benzol or chloroform, has been proposed by Richter[1] for the qualitative detection of lime, but its use is also restricted to perfectly fresh clinker which has not been exposed to moist air.

The Becke method for determining free lime from its high index of refraction as used by Wright[2] in his examination of the lime-silica series of minerals prepared by Day and Shepherd permits calcium oxide to be detected with certainty even in the presence of its hydroxide, but the method is not only tedious but extremely trying to the eyes, for it is necessary to focus on and examine individually each grain on the slide with a high power objective and feeble illumination.

PROPOSED TEST FOR FREE LIME.

The method here proposed for the detection of free lime is based on the formation on the slide of the microscope of a characteristic crystalline calcium phenolate readily recognizable in polarized light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent and adding a trace of water. The method of preparation preferred by the author is to dissolve 5 g. of phenol in 5 cc. nitrobenzol and add to this solution two drops of water. Instead of nitrobenzol, alpha brom-naphthalene may be used, and is for some reasons, notably its lower volatility, to be preferred. It does not, however, give such sharp results as nitrobenzol. Xylol gives good results as a solvent, but is too volatile and evaporates too quickly from the slide. The amount of water in the reagent may vary somewhat from the amount given. An anhydrous solution reacts very slowly. Too much moisture prevents the formation of good crystals and may also decompose the normal cement.

The solution may also be made to give a color reaction by dissolving 0.10 g. phenolphthalein in the above solution, but the presence of phenolphthalein hinders, and may sometimes prevent, the formation of definite crystals so that it is recommended to use a separate solution for the color test when that is desired.

In making this test about two or three milligrams of the finely powdered material are placed in the center of a microscope slide, a drop of reagent put upon it and then a cover glass, which is pressed down and rubbed gently to and fro till the cement spreads itself out somewhat. It is advisable not to spread the cement out too thinly but to leave a thick nucleus where the crystals will first appear, and to have the thickness decrease toward the edges. By this arrangement it is easier to get a rough approximation of the amount of lime present. The slide is now observed in a polarizing microscope with the nicols crossed, or if easier for the eye, with the polarizer rotated slightly. The author usually uses a two-thirds inch objective and one inch eyepiece giving a magnification of about 80.

The phenomena appearing when pure lime alone is being observed will first be described. When the freshly-prepared slide is put on the microscope the lime being isotropic is almost invisible and the whole field is dark. Within a few minutes the edges of the fragments of lime begin to show brilliant points which in a quarter of an hour develop

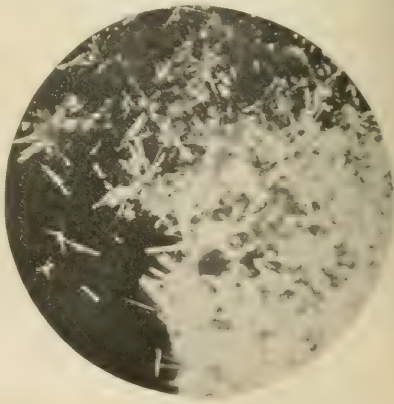


Fig. 1.

[1] *Thonindustrie Zeit.*, **1903**, 1863.
[2] *Amer. Jour. of Science*, **172**, 266 (1906).

into brilliant clusters of radiating needles as shown in Fig. 1 which is a photomicrograph of a commercial cement. On account of the great contrast in illumination between the brilliantly refracting calcium phenolate and the feebly refracting cement the photomicrograph shows nothing but the calcium phenolate crystals and does not show these sharply since their strong double refraction makes them appear to be surrounded by a halo. The eye of the observer at the microscope can readily discern the individual crystals forming what are only blotches of white in the photograph. If the lime fragments are crowded too closely together on the slide the crystals interlace so that their structure cannot be noted. These crystals grow till in the course of a couple of hours they may be 0.1 mm. long. Very little further change is noticeable for six hours, but in twenty-four hours the nitrobenzol will have largely evaporated and the crystals may have entirely disappeared. Confusion from formation of crystals of phenol has never been observed by us, the moisture present in the reagent or absorbed from the air probably preventing the phenol from crystallizing when the solvent evaporates.

Hydrated calcium oxide gives needles similar to the oxide, but they generally form more rapidly and are finer. On the other hand, the crystals formed from lime which has been fused in the electric arc have a different form. Instead of straight needles the crystals appear as plumes or feathery petals which in favorable cases give the group somewhat the appearance of a chrysanthemum. Something of this appears in Fig. 2 where the

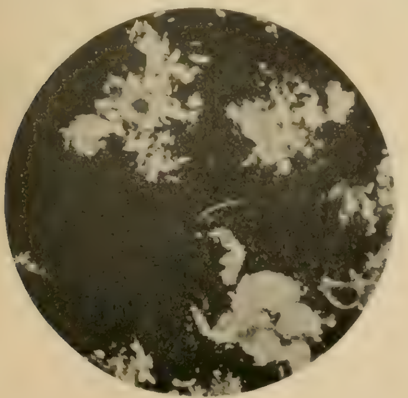


Fig. 2.

dark nucleus in the upper group shows the granule of free lime from which the plume-like crystals grew.

No substance other than calcium oxide or hydroxide has been found to give this reaction. Calcium carbonate does not give it. Burned dolomite does, but not burned magnesia, although it has been systematically tested for each 100° interval from 600–1600° C. Fused ortho-silicate of lime, $2CaO.SiO_2$, does not react with the reagent. Attempts to make a tri-calcium silicate which would not show free lime have, with one exception, been failures. It is not the intention here to discuss the much-mooted question of the existence of tri-calcium silicate in Portland cement, but it is within the scope of this paper to record that we have found that fused tri-calcium silicate always contains free lime, as reported by Day, Shepherd and Wright, and that tri-calcium silicate burned at lower temperatures usually contains free lime. We have, however, been able to prepare one sintered sample of the $3CaO.SiO_2$ composition in which free lime could not be detected by any test, which was hydraulic, and which stood a perfect boiling test of twenty-four hours. It is our belief that this represents an unstable condition, the free lime having been brought into solid solution, but final equilibrium not having been reached.

The solution containing phenolphthalein turns red in the vicinity of particles of lime within a few minutes. Usually crystals appear later. Calcium hydroxide also gives this reaction. Good Portland cement does not show any pink spots for several hours, nor does the one good sample of $3CaO.SiO_2$ which we have been able to prepare. On the other hand, magnesium oxide burned at temperatures of about 1000° C. gives almost as vivid a red as lime. We do not regard the indication from this solution as so valuable as those shown by the one without phenolphthalein.

FREE LIME IN PORTLAND CEMENTS.

With these experiments as a basis, the work was extended to Portland cements. Fortunately there were still on hand in the laboratory sealed samples of nearly all the cements made by Professor Campbell[1] in his studies of the constitution of Portland cement. With this abundant material at hand, it was a relatively brief matter to determine that free lime was always present in underburned cements, and that as the temperature of burning was increased, the free lime disappeared

[1] *Jour. Am. Chem. Soc.*, **24**, 248, 969; **25**, 1103; **26**, 1142; **28**, 1273.

as soon as a thoroughly clinkered and sound cement was obtained. Fig. 3 is a photomicrograph of such an underburned cement showing abundant

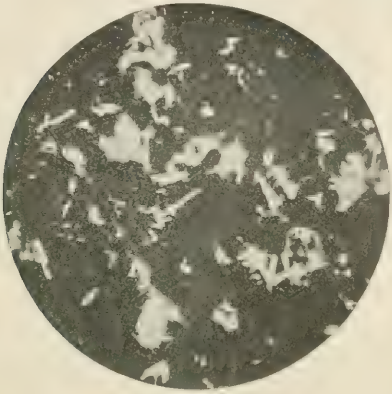


Fig. 3.

free lime. This cement disintegrated on the boiling test. The same cement when burned at a temperature 45° C. higher did not show any free lime and passed the boiling test perfectly. In an experiment at the time in progress in the laboratory where an attempt was being made to burn a very basic cement at the highest attainable temperature, it was possible to predict within ten minutes from the time the clinker came from the kiln that the cement would be unsound as it still contained free lime—a prediction confirmed by the boiling tests.

FREE LIME IN COMMERCIAL CEMENTS.

These laboratory tests afforded direct evidence of the correctness of the usual belief that a good Portland cement should not contain free lime. An examination of such normal commercial Portland cements as were at hand added a negative confirmation, as they did not show free lime. (Natural rock cement which is burned at a low temperature does contain free lime.) An investigation was then started to determine how far free lime might be the exclusive factor causing unsoundness in commercial cements, but as is frequently the case in pathological work, much difficulty was experienced in procuring specimens with a reliable history. Letters were sent to several of the large railroad and testing laboratories asking them to send the writer small samples of such unsound cements as came into their laboratories. It speaks well for the care exercised in the cement mills that the usual reply to our letter was a regret that they could not afford much assistance as very little unsound cement came into their hands. However, enough samples were sent to make the results of interest. Their discussion should be prefaced by the statement that the testing laboratories were requested to place one or two good cements with each lot of poor ones and to mark them all simply with a serial number so that they should really be unknown samples to the microscopist and that the method might receive an impartial test. The results of the boiling test were reported by the testing laboratory after they had received the report of the microscopic examination. The Michigan Technical Laboratory sent at different times sixteen samples, and the best idea of the applicability of the method may perhaps be gained by summarizing the results as determined microscopically and as subsequently reported by the testing laboratory.

COMPARISON OF MICROSCOPIC AND BOILING TESTS ON COMMERCIAL CEMENTS.

Cement No.	Microscopic report. Time in minutes before lime crystals appeared.	Remarks.	Report of boiling test by testing laboratory.
1339 A	10		Disintegrated
1339 B	69		Sound but weak
1339 C	7		Disintegrated
1340	None	Even after six hours	O. K.
1340 B	30		Radial cracks
1340 C	40		"
1341 A	10		"
1341 B	35		"
1341 C	30		"
7352	5	Small amount	O. K.
7357	9	Considerable	No cracks, but pats crumbled easily
7357 aerated	35	Not much	Sound but weak
7359	20	Considerable	Cracked and disintegrated
7362	35	Not much	O. K.
7365 A	60	"	Slightly weak
7365 B	30	"	Weak and crumbled easily

The agreement between the microscopic and the boiling tests is, on the whole, good. The microscopic tests detected all of the bad cements and afforded some idea of their relative inferiority. Where much free lime was evident within a half-hour the cement showed itself to be very bad when boiled. Where a longer time was required for free lime to show itself or where only a relatively few isolated crystals were detected on the slide, the cement was better, and graded up to one which passed the boiling test. Of the three cements marked O. K. on the boiling test, the microscopic test passed one (1340) as perfect, but condemned

the other two. Of these two, No. 7362 was reported as showing a little free lime in thirty-five minutes. Subsequent microscopic tests on this cement have shown several slides where free lime was entirely absent, so that it seems probable that the amount of free lime in this cement is so small as to be negligible. The third cement marked O. K. on the boiling test showed free lime very quickly, though in small amounts, and subsequent tests have never failed to show it. The discrepancy here must remain unexplained from lack of evidence, although a possible explanation might be found if it were known whether the cement had been aged at the mill. The influence of aging will be discussed later.

Another series of nine cements received from Dr. C. B. Dudley, of the Pennsylvania Railroad Co., is of interest because of the totally different nature of the report upon the microscopic examination, an extract from which is as follows: "None of them are very bad and I do not find the characteristic crystals of calcium phenolate in any of them. However A, C, D, F and H show rather too pronounced a color with the reagent, and I should be suspicious of their soundness, although with my present knowledge, I would not have ventured to condemn them as bad. Cements B, G and I seem perfectly good. Cement E is slightly suspicious." Dr. Dudley's reply is as follows: "The list of cements which we sent to you shows according to our record that A, B, C, D, E and F were what we call 'poor on boiling test,' while G, H and I were 'good on boiling test.' Your results seem to have picked out all the poor ones but one, and to have crossed in the case of one. I would like to say that these samples were not especially saved at the time the test was made but were taken from the records, so that there was always the possibility of samples being a little mixed."

Although this agreement was not altogether bad, it was disappointing to us for it did not seem as if the cements in question had shown enough free lime to cause unsoundness. Bearing in mind the possibility of aging having changed the cements, a boiling test was made on small pats, which came loose from the glass on twenty-four hours' steaming but were otherwise perfect. Futher correspondence with Dr. Dudley showed that there had been opportunity for the cements to age since the boiling tests had been made in his laboratory, so that the net showing for the microscopic test is considered a good one.

Another lot of cements interesting from the standpoint of effect of aging came in from the Osborne Engineering Co. Our report was as follows: "Nos. 1, 2, and 3 decidedly bad, No. 2 being perhaps the best; No. 4 bad, but better than the others; Nos. 5 and 6 suspicious, but hardly to be condemned." The reply of the Osborne Engineering Co. was as follows: "Samples Nos. 1, 2, 3, 4 and 5 were from different carloads of a brand of cement which we have been watching for some time. These five samples we had held in our laboratory for several weeks, making retests of them from time to time as they became more aerated, to see how long it would be before the samples would boil. Of them, samples Nos. 1, 2 and 3 do not boil yet, while samples 4 and 5 have recently passed our boiling tests successfully. Sample No. 6 is a sample of a different brand of cement which passed all our laboratory tests successfully." In this case, as in the others, the microscopic test picked out all the poor cements but was a little too severe on the good ones.

CAUSES OF FREE LIME IN PORTLAND CEMENT.

Taking the premise as established that free lime should be absent from Portland cement, it is in order to inquire how free lime comes to be present in cement. There may be two reasons: first, the lime in the raw materials may never have entered into combination with the silica, alumina, etc., or second, it may have entered into proper combination and been later separated out again in the free state.

Incomplete combination of lime in the cement is generally recognized as a common source of trouble. Temperature and duration of burning, and fineness of the raw material are all variables affecting this. It has been shown here that underburned cements always contain free lime and that at no period of the burning, up to the proper temperature, is free lime absent. But this proper temperature is influenced by the fineness of the raw materials, as was shown by Campbell[1] who, (Expt. 104) being unable to make sound cement in our laboratory rotary kiln from a stock raw mix furnished by a well-known Lehigh Valley mill even when the burning temperature was pushed to the limit of 1612° C., reground the mix in a jar mill and then was able (Expt. 105) to get sound cement at a temperature 137° C. lower. The lack of soundness in the first series he inferred must be due to free lime. Microscopic investigation of

[1] *Jour. Am Chem. Soc.*, **25**, 1103 (1903).

sealed samples from these earlier experiments has confirmed his diagnosis. Free lime is to be found even in the highest-burned specimen of Expt. 104. It is present in Expt. 105. No. 18 burned at 1451° which cement was not sound. Free lime is also, at the present time, to be found in the clinker of No. 19 burned at 1475° which in spite of its distinctly underburned appearance, was able to pass the boiling test. Clinker No. 20 burned at 1501°, however, shows merely the barest trace of lime, it being altogether absent from some slides, and from that point up to the highest temperature of 1627°, the cements are sound and free from lime. The microscope thus confirms the correctness of Professor Campbell's earlier conclusion. The Lehigh Valley mill was able, because of the longer exposure of the cement to high temperature in its kilns, to make sound cement from raw materials which our laboratory kiln could not handle. These experiments give a more exact demonstration of the fact known to all that coarse grinding of the raw mix produces bad cement, the disturbance being correctly laid to uncombined lime.

The possibility of free lime in cement being due to the separation of lime which had been once in a state of combination, is one which is not so generally accepted. We have already mentioned that we have made a material of the $3CaO.SiO_2$ formula containing no free lime, but that this material after fusion is found to contain free lime, as had been previously shown by Day, Shepherd and Wright. It is also known that overburned cement frequently dusts, a phenomena characteristic of the ortho-silicate of lime, $2CaO.SiO_2$. This ortho-silicate can have been formed from a compound richer in lime only through the dissociation of that compound with liberation of free lime. The evidence on this point is not yet conclusive, but is in accord with the hypothesis that cement is at least in part a solid solution whose viscosity even at the burning temperature retards chemical action to such an extent that equilibrium is not reached before the cement leaves the kiln. Portland cement is an unstable transition product. Were it to be heated till equilibrium was complete, it would not always be good cement.

AGING CEMENT CONTAINING FREE LIME.

Some data of the effect of aging commercial cements may be found in the report already given of the cements sent by the Osborne Engineering Co., where Nos. 1, 2 and 3 had been aerated in their laboratory for several weeks and were still unsound. They also contained free lime as shown by the microscope. Nos. 4 and 5 which had been aerated till they passed the boiling tests, still showed free lime with the microscope, but were reported as decidedly better than the others. This brings up the question as to whether the microscope can detect the difference between a cement which is unsound and one which, originally containing free lime, has become sound by aging. The question resolves itself into whether under ordinary conditions of storing, $Ca(OH)_2$ is ever present in appreciable amount or whether the conversion into carbonate is as rapid as the hydration. Experiments on aeration of cement in thin layers in the laboratory indicates that the conversion into carbonate goes practically as fast as the hydration and that a cement thus aerated will not be entirely sound until the microscope no longer detects lime. We have no evidence on the effect of aging cement in large piles, either as ground cement under cover or as clinker moistened or exposed to the weather. It is entirely conceivable that the latter procedure might give rise to formation of calcium hydroxide from even sound cement and cause erroneous conclusions to be drawn from the microscopic test.

SUMMARY.

The microscopic method here described is simple and reliable for the identification of even small amounts of free lime in Portland cement, but it is not a quantitative one. Cements which do not respond to this test within an hour can have no more than a harmless trace of free lime. Most of the sound commercial cements which have been examined show no free lime; a few have shown traces of it. The microscopic test is more delicate than the usual steam test, and cements which show some free lime under the microscope may successfully pass the standard tests for soundness but the pat will be weaker than if the cement were perfect.

Cement which comes from the kiln containing more than a trace of free lime will not pass the boiling test until the free lime has been removed. If the free lime is changed to carbonate by exposure to the air, the microscopic test will still give reliable indication of the quality of the cement. If, through method of aging, the lime remains as hydrate, the microscopic test alone might condemn a cement that had become perfectly sound. In the same way, a sound cement which had been wet, might be condemned from microscopic evidence alone.

Free lime is the chief cause of unsoundness in

Portland cement and, as every cement chemist knows to his sorrow, is exasperatingly liable to appear in spite of his care. It is always present in underburned cement. It is perhaps most frequently due to lack of fineness of grinding of the raw material. It may be present in overburned cement, where lime which had previously been combined may have been thrown out of combination at the higher temperature. With the boiling test as his only reliance the chemist must always work twenty-four hours behind his rotaries. The microscopic test should, therefore, have a wide range of usefulness in the mill as the test is so simple that it may be made, if desired, by the burner who can thus control his product hour by hour. The test should also be of value to the inspector who may, when it is necessary to make a quick decision, permit the use of those cements which show no free lime, and hold for further investigation the doubtful samples.

UNIVERSITY OF MICHIGAN,
Sept. 22, 1908.

NOTES ON ANTHRACITE PRODUCER PRACTICE.

By GEORGE C. STONE.

Received September 6, 1908.

The statement is frequently made that equal volumes of hydrogen and carbon monoxide have practically the same heating power; and this, not only in the advertisements of builders or producers, but in books and verbally by those who should know better.

It is true, that if equal volumes of hydrogen and carbon monoxide are burned and the products of combustion cooled to zero, the amount of heat liberated by the hydrogen is to the amount of heat liberated by the carbon monoxide as 100 is to 98.86, but such a condition never occurs in furnace practice. The water produced by the combustion of the hydrogen always leaves the furnace as vapor and the heating powers are:

$$H : CO :: 100 : 117.2$$

Then, too, the hydrogen flame is much shorter than that of carbon monoxide and it, therefore, tends to give a very intense heat close to the ports, but does not heat a large furnace as uniformly as the latter. This factor is often of more importance than the difference in calorific power. The makers of producers have encouraged the idea that hydrogen is equal to carbon monoxide for the reason that it is easier to run a producer with a large amount of steam as it prevents clinkering and saves much labor in poking. When the gas is high in hydrogen, in consequence of much steam having been used, it usually carries an excessive amount of water from undecomposed steam and this carries off much heat to the stack in consequence of its very high thermal capacity. It is, I believe, safe to say that most producers are given more steam than is economical. Enough must be used to prevent clinkering to a degree that interferes with the working of the producer, but anything in excess of that is detrimental to economy.

The calorific power of the gas, even when the water is figured as vapor, is not an accurate measure of its usefulness. Account must also be taken of its thermal capacity, of the amount of air required to burn it and of the composition and thermal capacity of the waste gases at the temperature at which they leave the furnace. In other words, a complete heat balance must be struck at working temperatures.

About three years ago, we increased the producers at one of our plants, by about three hundred per cent. and started a series of experiments to endeavor to improve our practice. At that time, we were using Taylor producers, seven feet in diameter. They were originally equipped with Bildt feeds, but these gave so much trouble by getting blocked by pieces of coal a little larger than usual, and gave such poor distribution with the fine damp anthracite used, that they were abandoned and a single plain feed hopper with bell was substituted. Number one buckwheat coal was used in these producers. The gas made is shown in column I of the table. The CO is low and the CO_2 and H very high; the gas is also very wet. This gas was unsatisfactory in the furnaces as with it it was very difficult to regulate the distribution of the heat.

We trained some boys to make gas analyses and set three of them to work on eight-hour shifts, making hourly analyses of the gas supplied to each furnace. The good effect of this was soon visible. As soon as the producer men realized that the superintendent knew what sort of work they were doing all the time, they became much more careful and the gas became more uniform in quality. The moral effect of regular analyses is wonderful, the men never know quite how much information the testing gives and are much less likely to neglect their work or to play tricks.

The next step was to reduce the steam very

largely. The result is shown in column II. The CO increased and the CO_2, H and H_2O decreased greatly. The calorific power dropped considerably, but the net calories (under working conditions) dropped very slightly. With the first gas over forty-nine per cent. of the heat went to the stack, with the second, only forty-seven. The net result of this change was an improvement in the furnace work, it being easier to regulate the heat with the high CO low H gas than with the other.

Up to this time, we had been burning number one buckwheat; we next changed to number two and for the first few days had a great deal of trouble to get good gas; but, by reducing the steam pressure and the thickness of the fuel bed and keeping after the men, in a short time we were able to make the gas shown in column III. This gas, still higher CO and lower CO_2, the H being about the same. The water is undesirably high, owing to the large amount of moisture in the fine coal, and the necessity of carrying more steam than we would like to, in order to prevent the clinkering of the high-ash coal. As will be seen, the calorific power and net heating power are higher than in the case of either of the others.

Shortly before changing to the smaller coal, we erected a number of Hughes producers, eight feet six inches in diameter. The shells of these can be revolved by power while the tops and ash hoppers remain stationary. The ash tables ordinarily revolve with the bodies but can be locked so that the revolution of the upper part grinds down the ashes. The revolving body enables a man to stand in one place and poke all parts of the producer as they come around to him. Each producer has two very small feed hoppers placed eccentrically. This arrangement of eccentric hoppers and a revolving body gives a very good distribution of the coal and to it our people at the works attribute much of the success of these producers. The gas made by these producers, as soon as we had learned how to run them, is shown in column IV. It contains considerably more CO and a little less CO_2 and about the same H and H_2O as the previous. The calorific power of this gas and its net effect are much higher than for any of the others.

Column V of the table gives the average gas made by three sets of producers from May 1st to 15th, 1908. It is still higher in CO and lower in CO_2 and H. It contains more water than it should on account of the very rainy weather during the two weeks of the run. Notwithstanding the excessive moisture, this gas shows the highest calorific power, the largest per cent. of useful

TABLE.

	I.	II.	III.	IV.	V.	VI.
Composition of gas, volume per cent.						
CH_4	0.32	0.30	0.50	0.40	1.00	1.00
CO	19.52	23.12	25.30	27.50	28.30	31.40
H	18.45	11.84	11.40	11.20	10.80	0.80
CO_2	9.56	7.88	5.50	4.50	3.60	3.20
N	38.17	51.04	49.40	49.00	46.60	63.60
H_2O	13.98	5.82	7.90	7.40	9.70	0.00
Air required to burn (25 per cent. excess).						
	1.17	1.08	1.15	1.21	1.23	1.08
Waste products, volume per cent.						
CO_2	14.83	16.43	15.87	16.12	15.81	18.55
H_2O	16.68	9.59	10.30	9.66	10.69	1.43
N	66.01	71.60	71.38	71.71	70.92	77.66
O	2.48	2.38	2.45	2.51	2.58	2.36
Heat balance of furnace.						
Sensible heat air at 15°	3.93	3.62	3.87	4.03	4.35	3.62
Sensible heat gas at 300°	76.06	71.85	71.71	71.32	72.77	69.92
Available calories in gas	805.39	758.69	811.59	850.42	906.20	777.92
Total calories entering	885.38	834.16	887.17	925.77	983.32	851.46
Calories in waste gas at 800°	436.98	391.75	426.97	434.63	455.82	407.61
Calories used in furnace	448.40	442.41	460.20	491.14	527.50	443.85
Per cent. of heat lost	49.35	46.96	48.13	46.95	46.36	47.87
Per cent. of heat used	50.65	53.04	51.87	53.05	53.64	52.13
B. t. u. per cubic foot	123.4	116.2	124.3	130.3	139.1	119.4
B. t. u. per cubic foot net	68.7	67.8	70.5	75.2	81.0	68.1
Relative volumes of gas for equal effects.						
Calorific power	112.8	119.7	111.9	106.8	100.0	116.5
Net effect in furnace	117.9	119.5	114.6	107.7	100.0	118.8
Net effect in furnace	100.0	103.7	97.5	91.4	84.8	103.2

effect and much the highest net heating power of any that we have made.

In column VI is shown the composition and properties of the gas from the blast furnaces smelting the residuum from the zinc oxide furnaces. It contains very high CO and an unusually large amount of CH_4 for an anthracite gas; the CO_2 is low and H practically absent, and it is absolutely dry. This gas is quite different from the ordinary blast furnace gas, owing to the zinc in the furnace charge which reduces the CO_2 and H_2O in the gas to CO and H, the reaction

$$ZnO + CO \rightleftharpoons Zn + CO_2$$

being reversible at the furnace temperature. This gas, if it could be delivered to the spelter furnaces at the same temperature as the producer gas, would equal the first two in net heating effect, and, I believe, would be a better and more economical fuel for our purposes than any of the producer gases. The dryness of this gas is an important factor. When saturated with water at as low a temperature as 15°, it loses about four per cent. of its net effect.

It is a curious fact that the useful effect in the spelter furnaces seems to vary almost directly as the CO and not as either the calorific power of the gas or as the net heating power under furnace conditions.

LABORATORY OF
NEW JERSEY ZINC CO.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 159.]

A COMPARISON OF THE CALCULATED AND DETERMINED VISCOSITY NUMBERS (ENGLER) AND FLASHING AND BURNING POINTS IN OIL MIXTURES.

By H. C. SHERMAN, T. T. GRAY, AND H. A. HAMMERSCHLAG.

Received October 1, 1908.

Those having to do with the mixing and testing of lubricating oils are aware, that while the specific gravity is practically an additive property in such mixtures agreeing approximately with the results of calculation by simple proportion from the amounts and gravities of the constituent oils, the same cannot be assumed to be true regarding other physical properties.

The object of the experiments here recorded was to determine in typical cases, the direction and extent of the differences between the calculated and determined viscosities and flashing and burning points in mixtures of heavy and light petroleum lubricating oils and of petroleum with sperm oil or with fatty oils.

VISCOSITY NUMBERS.

All of the determinations, here reported, were made by means of the Engler viscosimeter, usually at 20° C. but in two series at 100° C., and the results are expressed as "specific viscosity" numbers obtained by dividing the time of flow of the oil by the time of flow of water at 20° C.

First Series[1] *(T. T. G.).*

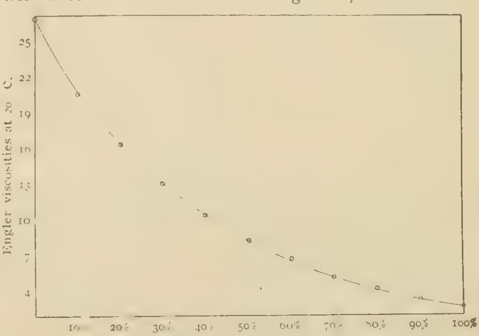
This series consisted of mixtures in tenths by weight of a high viscosity lubricating oil ("H") and a low viscosity lubricating oil ("L"), both made from Pennsylvania crude petroleum.

The Engler viscosity numbers were as follows:

ENGLER VISCOSITIES AT 20° C.

	Calculated.	Found.	Difference.
High viscosity oil ("H")	...	25.56	..
90 per cent. "H", 10 per cent. "L"	23.41	20.04	3.37
80 " "H", 20 " "L"	21.27	16.25	5.02
70 " "H", 30 " "L"	19.12	13.37	5.75
60 " "H", 40 " "L"	16.97	10.90	6.07
50 " "H", 50 " "L"	14.83	9.04	5.79
40 " "H", 60 " "L"	12.68	7.69	4.99
30 " "H", 70 " "L"	10.54	6.38	4.16
20 " "H", 80 " "L"	8.39	5.52	2.87
10 " "H", 90 " "L"	6.24	4.67	1.57
Low viscosity oil ("L")	...	4.10	..

In every case the viscosity of the mixture was less than the value obtained by calculation from the percentages and viscosities of the constituents. The difference between the calculated and determined values increased with the increasing proportions of light oil in the mixture up to 40 per cent. of light and 60 per cent. of heavy oil; with further increments of the light oil, the differ-



Percentage of lower viscosity oil.
Fig. 1.

[1] The different series of experiments are arranged for convenience of reference and comparison without regard to the chronological order in which they were performed.

ence gradually decreased. The determined viscosities are plotted in Fig. 1 (the viscosities as ordinates, the percentages of "L" as abscissae), and will be seen to form a very regular curve, dropping away from the calculated values somewhat more abruptly when the light oil is added to the heavy than when the heavy oil is added to light.

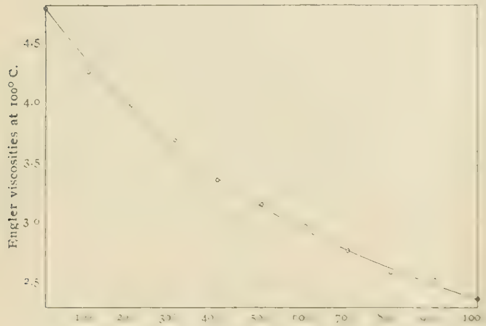
Second Series (T. T. G.).

In this case, mixtures, in tenths, of a high viscosity steam refined cylinder stock ("S") with a low viscosity steam refined black oil ("B"), were tested with the following results:

Engler Viscosities at 100° C.

	Calculated.	Found.	Difference.
Cylinder stock ("S")	..	4.96	..
90 per cent. "S", 10 per cent. "B"	4.70	4.39	0.31
80 " "S", 20 " "B"	4.44	4.10	0.34
70 " "S", 30 " "B"	4.18	3.78	0.40
60 " "S", 40 " "B"	3.92	3.43	0.49
50 " "S", 50 " "B"	3.67	3.22	0.45
40 " "S", 60 " "B"	3.41	3.04	0.37
30 " "S", 70 " "B"	3.15	2.80	0.35
20 " "S", 80 " "B"	2.89	2.61	0.28
10 " "S", 90 " "B"	2.63	2.51	0.12
Black oil ("B")	..	2.37	..

These results are shown graphically in Fig. 2. The general form of curve, here obtained, is the same as in the first series. That the individual



Percentage of lower viscosity oil.

Fig. 2.

results are less regular was thought to be due to the tarry matter which is usually present to a greater or less extent in steam refined cylinder stocks and black oils which have not been subsequently subjected to filtration or acid treatment. A similar set of mixtures was, therefore, prepared from filtered oils.

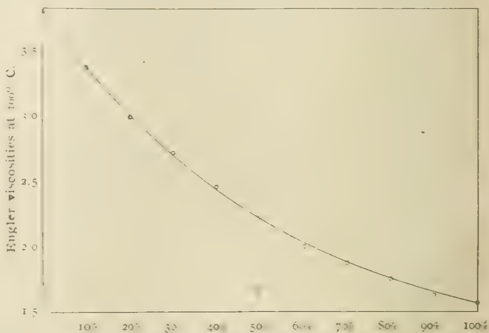
Third Series (T. T. G.).

The samples of this series were prepared from two well-refined petroleum lubricating oils, one of high and one of low viscosity, which are here designated "C" and "D" respectively. These mixtures were tested with the following results:

Engler Viscosities at 100° C.

	Calculated.	Found.	Difference.
High viscosity oil ("C")	..	3.86	..
90 per cent. "C", 10 per cent. "D"	3.63	3.41	0.22
80 " "C", 20 " "D"	3.40	3.02	0.38
70 " "C", 30 " "D"	3.17	2.75	0.42
60 " "C", 40 " "D"	2.94	2.49	0.45
50 " "C", 50 " "D"	2.72	2.24	0.48
40 " "C", 60 " "D"	2.49	2.02	0.47
30 " "C", 70 " "D"	2.26	1.88	0.38
20 " "C", 80 " "D"	2.03	1.76	0.27
10 " "C", 90 " "D"	1.80	1.63	0.17
Low viscosity oil ("D")	..	1.57	..

Here, as in the first and second series, the determined viscosity numbers are always lower than the calculated, but in this series, the greatest difference was in the mixture containing 50 per cent.



Percentage of lower viscosity oil.

Fig. 3.

of each oil, and the results when plotted (Fig. 3) form a curve which is more regular than the preceding.

Fourth Series (T. T. G.).

Prime neatsfoot oil ("N") was mixed in quarters by weight with a low viscosity lubricating oil ("E") made from Pennsylvania petroleum, and all were tested with the results which follow:

Engler Viscosities at 20° C.

	Calculated	Found	Difference.
Prime neatsfoot oil "N"	...	11.77	..
75 per cent. "N", 25 per cent "E"	10.33	9.69	0.64
50 " "N", 50 " "E"	8.89	8.19	0.70
25 " "N", 75 " "E"	7.44	6.83	0.61
Petroleum oil ("E")	...	6.00	..

These results are plotted in the lower part of Fig. 4, and show a curve similar to that of Fig. 3, but with relatively less difference between the calculated and the determined values.

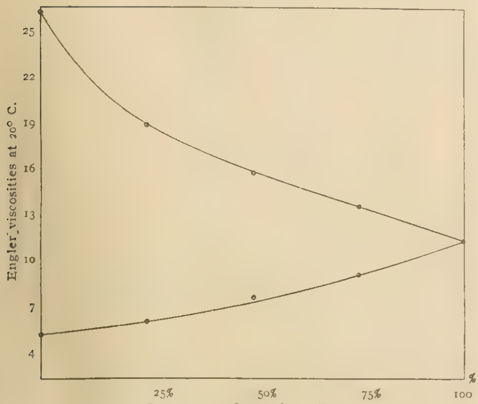


Fig. 4.

Fifth Series (T. T. G.).

Prime neatsfoot oil, the same as used in the fourth series of mixtures, was mixed in quarters by weight with the high viscosity lubricating oil used in the first series ("H") and the mixture tested with the following results:

ENGLER VISCOSITIES AT 20° C.

	Calculated.	Found.	Difference.
High viscosity petroleum oil "H"........	...	25.56	..
75 per cent. "H", 25 per cent. "N"......	22.11	18.60	3.51
50 " "H", 50 " "N"......	18.67	15.75	2 92
25 " "H", 75 " "N"......	15.22	13.65	1.57
Prime neatsfoot oil "N"................	...	11.77	..

Here the effect of 25 per cent. of the lighter oil upon the viscosity of the heavier was much greater than the effect of 25 per cent. of the heavier upon the viscosity of the lighter oil and this is true to such an extent that the difference between the calculated and determined viscosity is greater with 25 per cent. than with 50 per cent. of the less viscous oil in the mixture.

The results are shown graphically in the upper curve of Fig. 4.

Sixth Series (H. A. H.).

A different sample of neatsfoot oil ("Ne") and a different petroleum lubricating oil ("P") were mixed in quarters, by weight, and tested by another observer with the following results:

ENGLER VISCOSITIES AT 20° C.

	Calculated.	Found.	Difference.
Neatsfoot oil ("Ne")..................	...	11.94	..
75 per cent. "Ne", 25 per cent. "P"......	10.41	9.94	0.47
50 " "Ne", 50 " "P"......	8.88	8 22	0.66
25 " "Ne", 75 " "P"......	7.36	6.81	0.55
Petroleum oil ("P")..................	...	5.83	..

These results, if plotted, would give a curve similar to that of Fig. 3, but with smaller differences between the calculated and observed viscosities, probably because the difference between the constituent oils is much smaller.

Seventh, Eighth and Ninth Series (H. A. H.).

Mixtures of lard oil ("Ld"), of sperm oil ("Sp"), and cottonseed oil ("Ct"), with the same petroleum oil used in the sixth series ("P") yielded the following results:

ENGLER VISCOSITIES AT 20° C.

	Calculated.	Found.	Difference.
Lard oil ("Ld")......................	..	10.28	..
75 per cent. "Ld", 25 per cent. "P"...	9.17	8.72	0.45
50 " "Ld", 50 " "P".......	8.05	7.59	0.46
25 " "Ld", 75 " "P".......	6.94	6.55	0.39
Sperm oil ("Sp")......................	..	9.03	..
75 per cent. "Sp", 25 per cent. "P".......	8.23	7.98	0.25
50 " "Sp", 50 " "P".......	7.43	7.16	0 27
25 " "Sp", 75 " "P".......	6.63	6.43	0.20
Cottonseed oil ("Ct")...................	..	8.81	..
75 per cent. "Ct", 25 per cent. "P".......	8.06	7.82	0.24
50 " "Ct", 50 " "P".......	7.32	7.07	0.25
25 " "Ct", 75 " "P".......	6.57	6.33	0.24
Petroleum oil ("P").....................	..	5.83	..

These results are similar to those of the sixth series. In every case of mixed oil, the viscosity found is less than that which it would be if this were an additive property and in each of these four series, the difference between the calculated and determined values was greatest in the 50 : 50 mixture, but was only slightly greater in this case than in the 75 : 25 mixtures.

Thus, in mixtures of oils of different Engler viscosities, the viscosity of the mixture was found to be lower than the calculated value whether the mixture was that of two petroleum oils, a petroleum and a fatty oil, or a petroleum and a sperm oil; and in general the greater the difference in viscosities between the oils mixed, the greater was the difference between the calculated and determined viscosity numbers of the mixtures.

FLASHING AND BURNING POINTS.

First Series (T. T. G.).

This series was the same as that described as first series under viscosity determinations, being made up of mixtures by tenths of heavy and light lubricating oils both derived exclusively from Pennsylvania petroleum. The oils were tested in the Cleveland cup, the temperature being raised at the rate of 10° F. per minute and the test flame applied every 30 seconds. The results obtained, expressed as is customary in degrees Fahrenheit, were as follows:

	Flashing point.			Burning point.		
	Calculated.	Found.	Difference.	Calculated.	Found.	Difference.
Heavy petroleum oil ("H")	..	430°	..	..	495°	..
90 per cent. "H", 10 per cent. "L"	421°	405°	16°	485°	470°	15°
80 " "H", 20 " "L"	412°	390°	22°	474°	455°	19°
70 " "H", 30 " "L"	403°	375°	28°	464°	440°	24°
60 " "H", 40 " "L"	394°	375°	19°	453°	435°	18°
50 " "H", 50 " "L"	385°	370°	15°	443°	420°	23°
40 " "H", 60 " "L"	376°	360°	16°	432°	410°	22°
30 " "H", 70 " "L"	367°	360°	7°	422°	410°	12°
20 " "H", 80 " "L"	358°	355°	3°	411°	405°	6°
10 " "H", 90 " "L"	349°	345°	4°	401°	395°	6°
Light petroleum oil ("L")	..	340°	..	..	390°	..

Since the determinations of the flashing and burning points of lubricating oils in the open cup are subject to errors of 5° to 10° the irregular fluctuations in the difference columns above are not regarded as significant. For the rest of the work on flashing and burning points, mixtures by quarters instead of by tenths were considered sufficient.

Second, Third, Fourth and Fifth Series (H. A. H.).

Portions of the mixtures of petroleum lubricating oil with neatsfoot, sperm, cottonseed, and lard oils as used for the viscosity tests described above (viscosity series six to nine inclusive) were also tested for flashing and burning points in the Cleveland cup, but in the hands of a different observer and under slightly different details of manipulation, with the following results:

	Flashing point.			Burning point.		
	Calculated.	Found.	Difference.	Calculated.	Found.	Difference.
Petroleum lubricating oil ("P")	..	362°	..	..	398°	..
Neatsfoot oil ("Ne")	..	452°	..	..	550°	..
75 per cent. "Ne", 25 per cent. "P"	430°	406°	24°	512°	450°	62°
50 " "Ne", 50 " "P"	407°	384°	23°	474°	412°	62°
25 " "Ne", 75 " "P"	385°	370°	15°	436°	406°	30°
Sperm oil ("Sp")	..	538°	..	..	640°	..
75 per cent. "Sp", 25 per cent. "P"	494°	416°	78°	580°	456°	124°
50 " "Sp", 50 " "P"	450°	388°	62°	519°	420°	99°
25 " "Sp", 75 " "P"	406°	376°	30°	459°	410°	49°
Lard oil ("Ld")	..	592°	..	..	658°	..
75 per cent. "Ld", 25 per cent. "P"	535°	434°	101°	593°	496°	97°
50 " "Ld", 50 " "P"	477°	394°	83°	528°	446°	82°
25 " "Ld", 75 " "P"	419°	382°	37°	463°	422°	41°
Cottonseed oil ("Ct")	..	602°	..	..	665°	..
75 per cent. "Ct", 25 per cent. "P"	542°	420°	122°	599°	466°	133°
50 " "Ct", 50 " "P"	482°	390°	92°	532°	430°	102°
25 " "Ct", 75 " "P"	422°	378°	44°	465°	412°	53°

It will be seen from these results that in all four series of mixtures, including those in which two petroleums were mixed and those in which a petroleum product was mixed with a fatty or sperm oil, the flashing and burning points found were invariably below the figures obtained by simple calculation and the difference between the calculated and observed results was greatest in mixtures of one-fourth of the low-test and three-fourths of the high-test oil; in other words, the flashing and burning points are lowered by the presence of 25 per cent. of low-test oil to a much greater extent than they are raised by the presence of 25 per cent. of a high-test oil.

The difference between the calculated and observed flashing and burning points was found to increase with the difference in properties of the two oils constituting the mixture with the single exception that the differences in burning points of the petroleum-sperm oil mixtures were somewhat larger than for the petroleum-lard oil mixtures.

SUMMARY.

In mixtures of two petroleum lubricating oils or of a petroleum oil with a fatty or sperm oil, the Engler viscosity numbers and the flashing and burning points were invariably found lower than would be calculated from the percentages and properties of the constituents if it were assumed that these properties of oil mixtures were practically additive like the specific gravity.

In general, the difference between the calculated and observed results increases with the difference in properties of the two oils which constitute the mixture.

In some cases the difference between the calculated and observed results was greatest in mixtures containing equal weights of the constituents, but

more often it was greatest where a smaller proportion of the low-test or lighter oil was mixed with a larger proportion of the high-test or heavier oil.

A NEW BOMB CALORIMETER.

By Chas. J. Emerson.

Received August 27, 1908.

The whole scope of power engineering has for its basis fuel consumption. The rigorous attempts of late to develop and economize in all branches of power supply has led to a rather systematic investigation of the quality and relative merits of the several different forms of gaseous liquid and solid fuels. The exact heating value of fuels as determined by analysis or calorimeter test has passed from the stages of mere laboratory interest and has become an absolute necessity in the buying and selling of fuel in any considerable quantities. Users of large quantities of coal, lignite, peat, crude oil, light oils or what-not are determined to buy the same strictly upon their heat value.

The calorimeter test, probably the most accurate and satisfactory, is accomplished by means of the so-called bomb calorimeter. A small sample of fuel, carefully selected and reduced in bulk, by proper sampling, grinding and quartering (if a solid fuel) is placed in a strong receptacle and there burned completely, there being an excess of oxygen supplied. While the fuel is burning, the bomb is placed in a water calorimeter and the heat developed is measured in the usual way. There are several types of bomb at present in general use, differing principally in the method of supplying the oxygen. One type, that in which the oxygen is inserted as a gas under pressure, was originally inverted by Berthelot, and afterwards developed and refined for technical use by Mahler.

The writer has recently devised a new bomb of the Berthelot type, which has many novel features, being designed particularly to overcome some of the difficulties previously encountered in the use of this type of instrument. The determination of the heat of combustion of a fuel by a calorimeter test, if done by any of the calorimeters now in use, has required considerable manipulative skill, and although this element is not entirely done away with, yet the above-mentioned design has greatly reduced the standard of requirement regarding experimental ability. This bomb is also designed with a view of durability and to meet the exigencies encountered in an ordinary commercial laboratory. It is unlike previous bombs of the Berthelot type, as the receptacle instead of having one main portion with a cover, has its main portion divided and the two halves drawn together by a large nut. This design overcomes several difficulties of manipu-

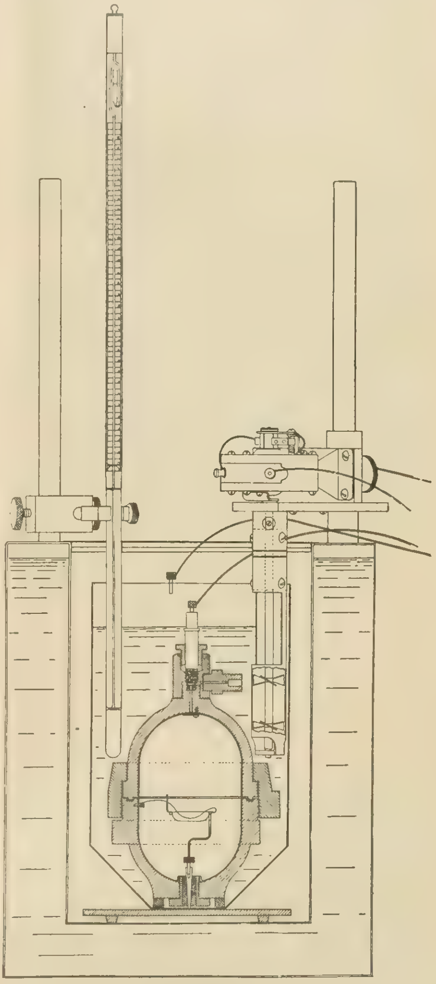


Fig. 1.

lation, giving easy access to the interior, making the adjustments easier, and facilitating the cleaning. The insertion of the lining, whether it be spun metal or porcelain, is done with greater per-

fection and accomplished more easily with this divided type of instrument. The operator can insert the fuse wire, platinum fuel pan and charge of fuel, with the lower cup in the bench holder, dispensing with any further moving of the pan, as is necessary where the pan is suspended from the cover, or is lowered into position after being filled.

The calorimeter can is tapered at the lower portion to conform to the general shape of the bomb, thereby reducing the quantity of water used in the calorimeter. This feature is always desirable, the reduction in the quantity of water used giving a greater rise in temperature in proportion to the heat developed. Any error in reading of the thermometer, or inaccuracies of the same becomes a smaller percentage error of the whole. The stirring is accomplished with a paddle stirrer in a depending tube, which is lowered into the calorimeter, the stirrer being driven by a directly connected motor. The entire testing outfit is designed with utility and durability in view. The piping which delivers the oxygen from the supply tank to the bomb, instead of being of flexible pressure tubing, is blocked out as a rigid piece, and unlike flexible tubing, it is practically impervious to the development of leaks (Fig. 2). The lower

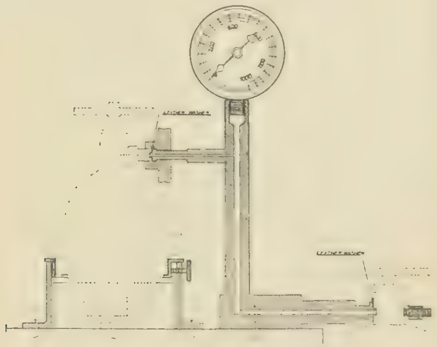


Fig. 2.

cup of the bomb is milled to fit a special holder, which does away with the possibility of jarring, which is liable when using a screw clamp, also dispensing with the manipulation of the screw.

The general principles of operation of this new type of bomb calorimeter are practically the same as others using oxygen gas under pressure. The charge of fuel is placed in the pan, the fuse wire having been previously wired into position. The upper half of the bomb is adjusted in place and the large nut brings the same home against a lead gasket inserted in a groove on the face of the lower cup. The bomb is then connected to the piping leading to the oxygen supply by means of the nipple on the valve at the top (as indicated in Fig. 2). The oxygen is allowed to enter the bomb until the gauge shows a pressure of 20 atmospheres. The spindle valve is closed at the top and the bomb is then ready for the calorimeter (Fig. 1).

Fuel bombs using oxygen gas under pressure, such as the above type, the Atwater, the Mahler, and others, might well be classed as standard instruments. The existing conditions in the calorimeter when the fuel is burning are such that practically no heat is lost. The composition of the fuel does not affect the accuracy of the work—the percentage of ash, water, sulphur, etc., not materially influencing the completeness of the combustion. The subsidiary heat-giving or heat-taking reactions, where impurities are encountered, prevalent in bombs of other types using chemicals to supply the oxygen, are here eliminated.

These pressure bombs will check each other with a given sample at hand, when operated properly—the only difference in the data involved is that of the constant of the instrument itself, which we term the water equivalent factor. This constant is properly determined by completely burning in the bomb a pure material whose calorific value is known. This substance should not be highly volatile and should be entirely free from chemically or physically combined water.

Comparative determinations made with the bomb described above and the Mahler and Atwater instruments show the following results:

Kind of coal.	Value as det. by Em. Fuel. Cal.	Value as det. by Mahler bomb.	Value as det. by Atwater bomb.
New river........	14985 B.T.U.	14880 B.T.U.	
New river........	14900 B.T.U.	14900 B.T.U.	
Pocahontas......	14950 B.T.U. 14915 B.T.U.		14910 B.T.U.

The agreement of the comparative determinations is extremely close.

[Contribution from the Food Division of the Bureau of Chemistry.]

THE MANUFACTURE OF OIL OF LEMON AND CITRATE OF LIME IN SICILY.

By E. M. Chace.

Received July 18, 1908.

The Island of Sicily is situated in $12\frac{1}{2}°$ to $15\frac{1}{2}°$ longitude east of Greenwich, $36\frac{1}{2}°$ to $38\frac{1}{2}°$ north

latitude. It is triangular in shape, the north coast running almost east to west, the east coast from north to south, the southern coast from northwest to southeast. The eastern portion in which the lemon-raising districts are situated is mountainous. The lemon-producing belt lies along the coast, the strip narrowing from a mile or two in width to a few yards, extending from Palermo to Messina along the north and from the latter city along the east to Syracuse. The belt is broken on the north coast at Termini, very little fruit being raised between that point and San Stefano and again on the east coast at Catania beginning again at Augusta, although between Lentini and Augusta lies one of the largest orange-growing districts of the island. While isolated patches of lemons may be raised in other parts, almost the entire output of lemon oil comes from this belt together with a small amount, less than one per cent. of the total, from Calabria. The lemon region naturally divides itself into five districts, three of which are contiguous.

Beginning at the southeast, the region around Syracuse, extending from Avola on the south to Augusta on the north, naturally separates itself into one district. It is less mountainous than those of the north and northeastern coasts and the fruit is raised further inland than in the other districts, one of the centers, Floridia, being from 12 to 15 miles from the coast. There are six centers here of which the city of Syracuse is the largest. Avola, Augusta, Priolo, and Melille are of lesser importance.

In the immediate neighborhood of the city itself are situated some factories of considerable size, at least one of which makes some pretense of using mechanical devices (in handling the fruit, not in the extraction of the oil). There are very few small factories such as are found in Catania, Messina and Palermo.

Floridia lies some 20 kilometers inland, the lowlands in the vicinity being given over to lemon culture. There are but four or five factories here of medium size with several smaller ones. Avola is situated near the coast about 25 kilometers south of Syracuse. With possibly one exception, these factories are small and poorly operated; considerable quantities of orange oil are produced here and much peel prepared for the production of Curacao. Both here and at Syracuse the chief products of the soil seem to be grapes, wheat and almonds. The next largest center is Augusta, 25 to 30 kilometers north of Syracuse on the coast. The single factory here is of medium size and produces both sweet and bitter orange oil in addition to lemon. Priolo and Melilli are unimportant centers between

Syracuse and Augusta. Both are inland towns the former containing two, the latter one small factory. There is also one other very small town, Solarino, situated near Floridia where oil is said to be produced. Altogether the district around Syracuse is one of no little importance. The reports of the British Vice-Consul, Mr. Lobb, for several years prior to 1905 show a production of about 25,000 pounds annually. In that year the amount rose to 80,000 pounds where it has since been maintained. The figures are for essential oils including lemon and sweet and bitter orange, no bergamot being produced. Being further south than the other districts, this region enjoys a milder climate and the production of oil begins sooner here than elsewhere. This may account for the fact that Syracuse oils are said to have throughout the year a slightly higher optical rotation than those from the other districts. The methods of production do not differ from those employed in the Etna and Messina districts.

Lentini situated about 20 kilometers south of Catania is an important orange-raising district; large quantities of the sweet varieties are shipped from here, but very little of the oil and no lemons are produced.

Further north, beginning at Catania and extending along the coast toward Messina, are the Etna and Messina districts, there being no definite natural boundary between them. It would seem highly probable that the oils produced in the two do not essentially differ, but the territory covered by them is of considerable size and great importance in the essential oil industry so that it is thought best to separate the districts for present purposes.

If the boundary of the Etna district is set at Giardini, the eastern coast is divided roughly between that district and Messina. The coast between Catania and Giardini comprises the finest lemon oil producing district of Sicily, containing the two largest centers of production in Aci Reale and Giarri besides very important points at Fiumefreddo and Giardini. Beginning on the south, Catania is one of the less important centers containing but one factory of considerable size with a few smaller ones scattered in the outskirts of the city.

North of Catania there are few factories, in fact, the city and its environs seem to form a small isolated district. The same is true of Aci Reale which is situated about 15 kilometers toward the north and about two from the coast. This is undoubtedly the largest center of production in Sicily, at least a dozen factories being situated in the town itself or clustered in the surrounding territory. They are both large and small and with one or two exceptions destitute of mechanical devices. The coast strip is quite wide here and the entire country seems given over to lemon culture. Giarre is but 10 kilometers further north, there being little territory given over a lemon culture between the two places. One factory of considerable size is situated here with perhaps two or three very small ones. Scarcely a mile from the town, however, at the railroad station for Mascali, is a small place known locally as Carrubba where are situated three or four large factories. One of these is the largest and best equipped in the island. It is perhaps, indeed, the only well equipped place containing mechanical carriers, stirring machines, aerial railway for carrying off waste products, and electric lighting plant, machine shop, etc. Machines for extracting oil had been installed here but later abandoned for the sponge process. At the height of the season, this place employs some three hundred hands, sorters, cutters and spongemen included, and produces 200 to 250 pounds of oil per day. The neighboring factories are not so large, employing roughly about fifty hands each. Altogether the district including Giarre is one of the largest producing districts in the island. The town of Mascali is situated above this place on the side of Mt. Etna, drawing its supply from the valleys and hilltops surrounding it, the lemons apparently being grown on high land which is unusual. The four or five factories situated there are small.

Catania, Aci Reale, Giarre, Mascali and perhaps Fiumefreddo are situated upon decomposed lava beds of Mt. Etna. From Giarre north to Giardini the whole coast line is a continuous lemon grove with numerous factories, large and small, scattered through it. At Fiumefreddo are three or four of fair size and at Giardini one probably second in size in the Etna district. The latter factory produces large quantities of both sweet and bitter orange oil, which is unusual in this district although oranges are raised at Paterno, Aderno, and Bronte situated well up on the slopes of Etna and at Francavilla further north nearer Giardini. The produce of this district goes chiefly to an Essential Oil Producers' Association and is sold by them to Messina brokers so that little or no data relative to the output is obtainable. The city of Catania is its chief port, but only a

few hundred pounds, usually less than a ton of essential oils, are exported from that point which would not represent the output of the city itself. The methods used in the Etna are not different from those used in the Syracuse and Messina districts.

Taking the northern boundary of the Etna district as Giardini, the Messina district would begin at Letojanni following up the east coast to the city of Messina and including several minor centers on the north coast as far west as Rometta. Here again, from Letojanni to Messina, the whole coast line is a continuous lemon orchard with but slight interruption in the neighborhood of Ali. Factories are, of course, scattered throughout, the coast strip being much narrower than in the Etna district. At the southern end the important centers are Santa Teresa and Roccalumera which are practically one town. Taken together they are probably second in importance only to Aci Reale in the Etna district. Their factories, six or eight in number, are of considerable size but as a rule are not well equipped. Nearer Messina, the towns of Galati, Tremestieri and Gazzi all contain large factories. The coast strip is narrow here and the fruit is largely shipped in from the inland valleys and from further south. The factories are, as a rule, better equipped than those in any other part of the island. At Messina proper, there is but one large factory which is probably second in size in the country. It is well equipped and draws supplies of fruit from considerable distances on both sides of the city. The city contains numerous small factories wretchedly equipped and situated; often the fruit is cut, washed in the streets and the oil extracted in the living rooms of the houses. This condition is not confined to this city, by any means, but is generally prevalent in all of the large cities and in many of the smaller towns, the great majority of the smaller factories being sordid and filthy in the extreme and, indeed, so are some of the larger ones.

On the north coast 12 kilometers west of Messina is a center of some importance, Bauso. The factories are 3 or 4 in number and of fair size. The smaller towns of Rometta and San Andre also contain small factories as do the towns of Letojanni and Scaletta on the south coast.

The city of Messina itself is the center of the essential oil trade for Sicily, a very large percentage of the oil produced being exported from here. The British consular reports credit the port with a total exportation of essential oils of between four and five hundred tons annually.

Formerly, a considerable quantity of oil was produced in Messina from the culls of stored lemons. The sound fruit was carefully packed during the season and stored for shipment after the season for fresh fruit was past. Naturally, when the time for shipment came, many of the lemons had developed defects and were sold to oil factories. Their chief value probably lay in the citrate of lime produced from them as they would contain but little oil, and that abnormal. This practice has greatly decreased recently, owing to the increased production of summer lemons.

To the west of the Messina district along the north coast is situated the important center of Barcelona. There are seven or eight factories here, both large and small. The district is unique, owing to the fact that the three-piece method of production is used. A short distance west of Barcelona is a town of considerable size, Patti. Here two factories are located, both below the average size, one of them producing besides lemon oil, both sweet and bitter orange oil. For considerable distance further west only isolated orchards of lemons are seen. At Naso there are a few small factories and again at Santa Agata.

These towns along the north coast are hardly large enough to be called districts. With the exception of Barcelona, their production is a very limited one. It is quite possible that the oils produced are typical both on account of the geographical location and the methods of production used. The finished product of the district is sold to Messina buyers, none being exported directly. Continuing west toward the Palermo district, the mountains soon come down to the sea so that no orchards are seen after passing Santa Stefano until Termini is reached. The latter place is about forty kilometers from the city itself and may be regarded as the eastern boundary of the district, although no manufacturing centers of importance are found until the neighborhood of Bagheria is reached, some fifteen kilometers from Palermo. Here, at the small town of Ficarazzi, is a center containing one large and several smaller factories. The district may be said to extend from this point to Partinico, a town some twenty kilometers southwest of Palermo and six or seven kilometers from the coast. The region is not a continuous lemon grove as is the case on the south, but rather contains large isolated groups of orchards, one of the

largest being on the Conce d' Ora, the valley extending from Palermo to Monreale. There are some eight factories there, the largest claiming an output of twenty thousand pounds annually. Palermo itself contains several large, apparently well-equipped factories. Carini, Cinisi and Partinico are small towns on the Palermo, Trapani railroad line of little importance. Carini has but one or two small factories, Cinisi but one. Partinico has some two or three, one of fair size. The methods of production used in all these places are similar and are said to have been introduced from Barcelona, from which place many of the operators originally came. The three-piece method is universally used and it is a common practice to distil foots.

A possible cause for abnormal oil in this region is the large number of summer lemons produced here. To produce this fruit, the lemon tree is allowed to blossom as usual in the spring. In July and August as soon as the fruit has set, the roots are uncovered, causing the tree to wilt and drop a great part of it. When the wilting has gone on sufficiently, the roots are recovered, the tree irrigated and heavily manured. This change in treatment causes it to regain its former state, and in so doing, it puts forth a fresh crop of blossoms from which lemons mature the following summer at a time when the old crop is exhausted and the supply is being drawn from the storage stock. The prices obtained are usually sufficiently high to pay for the trouble, loss of fruit in the natural crop and injury to the tree. This fruit is known as "verdelli." If the prices are low, or if for any other reason the crop is not gathered but remains upon the tree until the following natural crop is gathered, it becomes "bastardoni." This practice is most largely followed in the Palermo district, while the raising of the "verdelli" takes place in nearly the whole island wherever lemons are grown. This is the only district in which oil is made from the culls. When the price of verdelli is low, larger quantities of oil are made so that at times it might become a factor in making an abnormal product.

The season in the Palermo district begins fully six weeks later than at Syracuse and continues well into the summer; the produce is both exported and sold to Messina buyers. There is very little, if any, trade direct with the United States. The British Vice-Consular reports credit Palermo with a total exportation of essential oils of about 100,000 pounds annually.

It is an extremely difficult matter to obtain data upon which to base conclusions as to the relative importance of the different districts of Sicily; the information furnished by factory owners is extremely unsatisfactory, in many cases amounting to mere guess work. It is certain, however, that the territory comprised in the Etna district produces the largest quantity of oil, the territory in the Messina district is probably next, while Palermo, Syracuse and Barcelona are of lesser importance, Palermo coming first with the other two of about equal importance.

Two methods of producing lemon oil are in use in Italy, the sponge method, by which all of the oils of Sicily are made, and the machine method. which is used only in the mainland. Over 99 per cent. of the oil produced is made by the first. The one most used, the two-piece method, is worked as follows: The lemons are cut in halves, this part of the work being done chiefly by children or

Fig. 1.—Cutting the fruit, two-piece method.

women, the cheapest kind of labor. An ordinary paring knife is used and the fruit divided from end to end or crosswise, usually the former method only when it is intended to make some use of the skin after extracting the oil. The work is carried on with great rapidity where the fruit is cut crosswise, the knife being started through the rind, and the lemon cut in two and thrown into the storage tubs by one motion of the arm. The tubs containing the cut fruit are dumped into shallow troughs. Here the pulp is separated from the skin. Older girls and women are employed for this work almost exclusively. A spoon-shaped instrument is used, being inserted between the pulp and rind and with one twisting motion forced toward the end of the fruit when with a quick jerk the pulp is pulled from the rind and deposited in the trough. The rinds are thrown into baskets, and before being carried to the spongers are thoroughly soaked

in water, usually by immersing the entire basket in a large tub or reservoir and shaking off the excess. They are then allowed to remain some four

Fig 2.—Removing the pulp, two piece method

or five hours, or even over night. All producers agree that this results in obtaining a larger yield than where the skins are worked immediately after the pulp is removed.

The extraction is done entirely by men, rarely are women employed, as the work is quite laborious. The workers sit upon low stools, the skins being dumped upon the floor in front of them, and a basket for the exhausted skins set a little to one side. A small earthenware bowl, eight to ten

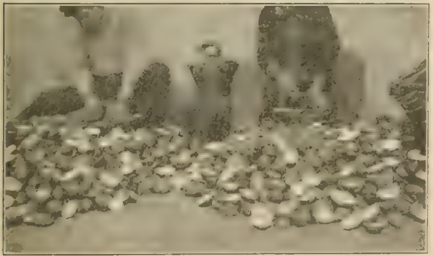


Fig 3 —Extracting the oil, two piece method

inches high and of about the same diameter, is placed on the floor between the workman's feet. This bowl has at one side a lip directly beneath which is a small concave depression which serves to hold back the residue when the oil is poured from it. Across the top is placed a round stick of wood about an inch in diameter, so notched as to fit the widest part of the bowl. Across this stick is hung a flat sponge surmounted by another thicker one and finally a third, which is cup-shaped. Into this latter the lemon skin is inserted with the right hand, the left being used to press upon the sponge, the weight of the whole body being thrown into the motion. The lemon rind is then turned partly over and the pressure renewed. This is repeated some three or four times after which the skin is thrown into the waste baskets. Each half lemon rind has to be handled separately, receiving three or four pressings. It takes from 1600 to 2200 of these halves to produce one pound of oil, the quantity depending upon the size, ripeness and freshness of the fruit. It is said that green fruit produces rather more oil than ripe, and that the fruit should be worked up as soon as possible after picking. A good workman can produce between two and three pounds of oil per day, for which he receives forty to sixty cents.

By the two-piece method only a small quantity of water is expressed with the oil and the process of separation is very simple, the bowl being tilted forward until the oil can be blown from the surface over the edge into another receptacle. The water and residue remaining behind are separated from the traces of oil by the same means and finally filtered through felt bags. The residues left in these bags are collected for several days until a sufficient quantity are on hand when the bags are placed under a hand press and freed from the last traces of oil.

The three-piece method used in the Palermo and Barcelona districts differs from the method just described, mainly in the preparation of the skins before pressing. The rind is pared off in three slices, leaving the greater part of the pulp with some little rind at the ends. The paring, as a rule, is done by boys or men and the skins are washed or soaked as in the two-piece method.

Fig 4.—Paring the fruit, three-piece method.

The sponging method used differs but slightly; the pieces being smaller are not inserted in the cup-shaped sponge but pressed flat against a large

Fig. 5.—Extracting the oil, three-piece method.

sponge placed over two others as in the first method. The earthenware bowl is always used, sometimes the oil being pressed directly into it; in other cases it is supplemented by a white glazed bowl which is set upon it. The sponge stick is fitted to this and the oil received directly here. The larger bowl is used only for the separation of oil and residual juice. A much larger amount of pulp is left adhering to the skins by this method so that the juice expressed with the oil is very much greater than by the other method. The claim is made, however, that oil made in this way filters much more rapidly and remains clear longer. The explanation given is that more of the oil-soluble materials are coagulated by the citric acid and are thus more easily removed and do not precipitate out later.

The use of machines in producing lemon oil is confined to the province of Calabria. The oil thus produced is but a very small part of the total product. It has a deeper color than the sponge oil and is used to deepen the color of the latter when produced late in the season. The machine used is extremely crude. The lemons, about eight in number, which must be of a uniform size, are placed in the receptacle between two grinding discs. The lower of these discs is stationary, the upper one being turned by an arrangement of wooden cogs against the side fly-wheel. The pressure exerted by the weight of the upper disc is partly compensated by the arm at the rear which is also used to raise this part of the machine, so

Fig. 6.—Calabrian lemon oil machine.

that the fruit may be placed in position and removed. A small bell is arranged so as to ring after so many revolutions of the flywheel, usually about one-half minute being required to remove the oil-bearing part of the lemon skin. The fruit is then removed and carefully wiped with a sponge, the greater part of the oil and gratings having been collected in a receptacle placed under the lower disc. The mixture is filtered through cloth filtering bags, the oil and water being separated by blowing the latter from the top. The filter bags containing the final residue are pressed under hand-presses similar to those used in Sicily. The oil produced is of a deep rich yellowish color and is used solely for the purpose of bringing up the color of pale oils. It is sold to Messina buyers.

A machine differing very materially from that used in Calabria has been introduced into some of

the larger and better operated factories in the Messina and Etna districts. Its use has, however, been abandoned, the operators claiming that the machine was expensive to operate and did not extract as much oil as did the sponge method.

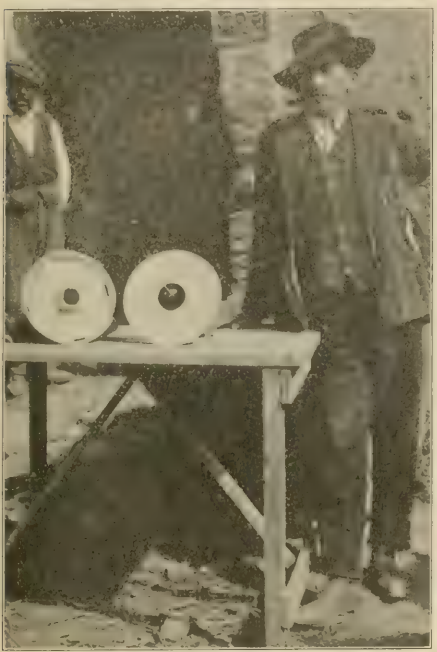


Fig. 7.—Discs used in the Calabrian machine.

The method of preparing the fruit for use on this machine was the same as for the two-piece method so that the only labor-saving was among the spongers. The Calabrian machine does not require any preparation of the fruit but (on the other hand, does not work over six or eight lemons at a time) requires three attendants and works badly on uneven fruit, requiring lemons of practically the same size for each load.

Of the sponge methods, the three-piece has the seeming advantage of eliminating the necessity of removing the pulp from the rinds. It is claimed, however, with some apparent reason that this saving is more than overbalanced by the increased time required in the paring and in the sponging process. It has also an additional disadvantage in that the skins have a considerable amount of adhering pulp, and therefore must be sent to the juice presses after the oil has been removed, increasing the work in this department of the factory.

In the Barcelona and Palermo districts the residue or fece is distilled instead of filtered. It is collected as described under the two-piece method, diluted with water and distilled from a small copper (alembic) still. This still consists of a large pot holding two or three gallons and a condensing basin. The latter fits loosely over the top of the former, the joint being closed by clay. The

Fig. 8.—Still used on residues in the Barcelona district.

water from the basin can be drawn off through a short tube which runs into the water compartment of the basin, while the larger or condensing tube entering the lower chamber is wrapped with wet clothes to assist the condensation. The distillate is collected in a bottle contained in an earthenware bowl. In this way the oil and water are roughly separated; as the bottle is filled with water, the oil runs over into the bowl. The product has a disagreeable odor and none of the fragrance of the natural oil. As has been stated, the use of these stills is confined so far as was discovered, to Barcelona and Palermo. Brokers who purchase oil from manufacturers usually have a clause in their contracts, which stipulate that the oil delivered to them shall not contain over 5 per cent. of the distilled product. As a matter of fact, however, the manufacturer saves his residues until he has sufficient quantity to keep his still going for several days when he commences to work them up. The next lot of oil sold after this distillation is very likely to contain all of the distillate produced from those residues. Many brokers in Palermo do not allow any distillate in

the oil which they buy as pure, but they do contract to take at the same price, a quantity of it not to exceed 5 per cent. of the pure oil. In other words, they prefer to do the mixing themselves. The trouble here is that 5 per cent. of distilled oil added to the sponge oil is not detectable with certainty in the cursory examination made by the brokers' analyst so that very often he not only buys the 5 per cent. in a separate package, but another five already mixed in by the manufacturer. The oil from all the processes is finally filtered through paper and stored in large copper tanks.

The manufacture of citrate of lime is almost universally co-existent with that of lemon oil. The concentration of lemon juice is practiced in a few plants at Santa Agata and Reggio but the amount of juice used is very small in proportion to the vast amount used in the citrate manufacture. Nearly all lemon-oil producers, even the very small ones, manufacture for themselves and a very few sell to larger factories. The process is very simple, requiring an inexpensive installation of apparatus and practically no skilled operators. When the by-product (the lemon pulp) from the lemon oil manufacture is received it is first run through a crushing machine in order to break the partitions and cells. The machine usually consists of a wooden hopper leading on to two wooden rollers set at proper distance. A chute leads from these rollers under which are placed receptacles for receiving the pulp. Arrangements are also made for receiving the drippings and conducting them to a central storage tank. In a very few factories this crushing machine is run by steam power, the greater number of places using hand-power.

Fig. 9.—Hand crusher used for preparing lemon pulp.

The pulp is now shoveled into large woven straw filtering mats, and packed down as tightly as possible by means of wooden rams. These mats are placed in position, one on top of the

Fig. 10.—Hand-presses used for expressing the juice from lemon pulp.

other, in upright presses. In some places the presses take only four or five mats, in others as many as a dozen. In the smaller factories they are extremely crude, some even having wooden screws. In all cases they are set down by hand-power, the final turning of the press being aided by a windlass. The juice from the crusher and presses is collected in a central storage tank from which it is pumped, usually by hand, into a large wooden reservoir. These reservoirs are heated either by steam coils or by passing steam directly into the juice. When hot, it is neutralized with lime water, while being thoroughly stirred. The end-point of the neutralization is found by means of litmus paper. After standing hot for some two or three hours, the precipitated calcium citrate is drawn off into a tank having a false bottom covered with a heavy porous cloth upon which the citrate deposits and through which the waste fluids filter off. When sufficiently dry, the citrate is shoveled into small filtering bags which are placed under a hand-press and the excess of moisture removed by pressure. The product is then removed from the

bags and placed in iron trays, these trays being placed on racks in a closed room containing a charcoal burner. In this manner they are dried

Fig. 11.—Vat used for precipitating citrate of lime.

down to a moisture content of a few per cent. The product is packed in hogsheads and shipped largely to the United States and England.

TURPENTINE AND ITS ADULTERANTS.

By Arthur E. Paul.

Received September 18, 1908.

In the turpentine forests of our southern states the custom is to cut a cup-shaped opening or "box" into the pine tree, about 11″ across, 3″ wide, and 5½″ deep, having a triangular, or "V"-shaped, upper surface. As this upper surface—commonly called "rabbit's ear"—"bleeds," the juice, of about the consistency of glucose, runs into the "box" and is collected. At the end of a week the upper surface is cut afresh ("streak"), and such a new "streak" is cut every week for a season of nine to eleven months. The gum so obtained during the first year is called "virgin gum," and the opening made is called "virgin box."

The height of this opening is now some 18″ to 24″. During the second year, the cutting of streaks is continued as before, but the opening is now called "yearling box," and the product "yellow dip." During the third year the opening is termed, in the east, "buck box," and in the west, "doe box." After the third year, the opening is called "pulling box," and the product is still "yellow dip." We have then: "yearling box yellow dip," "buck box yellow dip," "doe box yellow dip," "fourth year yellow dip," etc.

During all this time some of the gum hardens and adheres to the tree. This is scraped off, and is known as "scrape," or as "gum thus." When the "Herty" system is used, the gum, instead of running down into the "box," is—by means of two pieces of steel placed at an angle to each other and driven into the tree—made to run into a cup, hung just below the streak. In this system the product, from year to year, is practically "virgin gum."

All the products mentioned above: virgin gum, the various yellow dips, and gum thus, are called "crude turpentine" or "gum turpentine."

The scientist, however, designates these substances collectively as "turpentine." In fact, his definition of the word is: "the oleo-resinous exudate from certain species of 'Pinus'."

By distillation, in the presence of water, this gum is separated into the non-volatile "rosin," and the volatile mixture of hydrocarbons, which is known scientifically as "oil of turpentine," and commercially as "spirits of turpentine," or more commonly, simply as "turpentine," and vulgarly as "turps," and sometimes, especially to distinguish it sharply from so-called wood turpentine, it is called "gum turpentine."

To recapitulate:

Scientific term.	Commercial term.		
Turpentine.........	Crude turpentine. Gum turpentine.	Virgin gum.	Various kinds.
		Yellow dip.	
		Gum thus. Scrape.	
Oil of turpentine....	Spirits of turpentine.		
	Turpentine.		
	Turps.		
	Gum turpentine.		

There is, then, some confusion in the use of the word turpentine, but scientific and commercial usage agree in applying the term only to the oleoresin referred to, or to the product derived therefrom.

In this paper, the word will be used in its commercial sense, *i. e.*, it will refer to the distillate from crude turpentine.

Turpentine is used in the manufacture of paints and varnishes. Its value, according to tradition, is due to its property of acting as a carrier of oxygen, thus aiding in the hardening of the oils and gums used. The correctness or fallacy of the theory has not yet been satisfactorily established.

Turpentine consists very largely of the hydrocarbon "pinene," and to a smaller extent, of "cymene." The former is readily polymerized by sulphuric acid, the latter not.

Specifications.—Because of the scarcity and comparatively high price of turpentine, and its liability to adulteration, the importance to the consumer, of assuring himself of the purity of the goods purchased, is apparent. Many large buyers, being aware of this fact, buy on specifications. These generally include a list of limits of physical constants, supposedly peculiar to turpentine. The specific gravity, flash point, behavior on distillation, polarization, color, residue on evaporation, and insolubility in sulphuric acid, are the most common limitations. The specifications also generally include a statement requiring the turpentine to be "pure."

Of these, all but the last-mentioned clause are superfluous—the object of the specification not being to secure a certain *quality* of goods, but merely to exclude the possibility of sophistication, and are virtually methods for establishing purity. The "total solids" *may be* an exception, as they vary somewhat even in pure turpentine, and it *may* be well to specify limits, as they *may* be indicative of quality.

Wood Turpentines.—This designation is really a misnomer, since these products are not included in the definition given for turpentine. However, they are used in place of turpentine; according to most consumers, they answer the purpose equally well, and are of similar composition. Moreover, their use has become quite general, and they have been, and are, commonly designated as wood "turpentine."

Again, we must bear in mind that, because of the destruction of turpentine forests by methods of collection now in vogue, future dependence for turpentine supply will probably rest with wood turpentine.

Three markedly different varieties are at present manufactured:

"Stump" turpentine is made by destructively distilling stumps or other parts of dead resinous pine, or the so-called light wood. The products are wood alcohol, pyroligneous acid, tar, charcoal, and crude wood turpentine. This last, upon refining, yields a product which, but for its pungent, empyreumatic odor, is considered by users a very good substitute for turpentine. It contains considerable pinene, and notable quantities of cymene, more, indeed, than does "turpentine."

Steamed wood turpentine is made by distilling fat chips with steam and refining the distillate. The character of the product depends upon the kind of chips used, and more particularly upon the care exercised in its manufacture. Some specimens are in no way superior to the "stump" variety, while others are hardly distinguishable from true "gum" turpentine, the odor being very similar, in fact, more pleasant, and less pungent; and as to physical constants and chemical composition, they are practically identical therewith.

The third variety is interesting rather than commercially important, the output at the present time being insignificant. It may be called "*Wood Pulp Turpentine*," being a by-product in the manufacture of spruce or other wood pulp. That from spruce is composed almost entirely of cymene, which is an isomer of pinene. Its physical constants are similar to those of turpentine, but it is only very slightly affected by concentrated sulphuric acid. Its odor is strong and peculiar, but is really less pungent and less offensive than that of any of the other varieties, even the real "turpentine."

Since the only objection to wood turpentines, raised by practical users, is the odor, and as their price is but very little below that of turpentine, it follows that as a commercial adulterant they would have to be used in large quantities, so large as to be easily recognized by the odor. Notable quantities will be frequently indicated by the greater per cent. of total solids, the greater distillate from sulphuric acid in the method given below and the greater residue from direct steam distillation. Fractionation too will show a wider range of boiling points. Many specimens, especially of the "stump" kind, give distinct tests for rosin spirits.

Rosin Spirits.—This includes the lighter fractions obtained during the distillation of rosin, in the manufacture of rosin oil. It is commonly mentioned in treatises on paints and so forth, as one of the adulterants of turpentine. While it

may be so employed, the writer has failed to find any evidence thereof, either analytically or commercially. For its detection the method of P. H. Conradson[1] is the most satisfactory, and nothing better can, at present, be suggested.

Petroleum Products.—Whatever may be the relative merits of the various kinds of turpentine, and whether the virtues ascribed to them are real or imaginary, the fact remains that they have certain distinct physical properties, and command certain market values, none of which are shared by any of the petroleum products. However, some of the latter have certain physical properties in common with turpentine, so that they are frequently employed by unscrupulous dealers for the purpose of adulteration. The number of turpentine substitutes now on the market, is legion. They consist almost invariably either of petroleum products pure and simple, or mixtures thereof with turpentine, wood turpentine, asphalt spirits, or similar products. Petroleum products are usually chosen, having a range of boiling points within that of turpentine.

Among the best known of these are:

"Turpalin," price about 20 cents per gallon.

"Terrabentine," price about 20 cents per gallon.

"Sunoco Spirits," price about 15 cents per gallon.

"Chicago Turpentine," price about 30 cents per gallon.

"Norway Turpentine," price about 40 cents per gallon.

"Nuturps," price about 40 cents per gallon.

"Turpteen Spirits," price about 30 cents per gallon.

"Varnish Turpentine," price about 40 cents per gallon.

"Erco Spirits," price about 15 cents per gallon.

Whatever may be the relative desirability of turpentine as compared with petroleum products, the consumer should *know* which he is using. If he is satisfied with the properties of kerosene for his purpose, it will be economy for him to buy it as such, at the market value thereof. If he prefers to pay the extra price for turpentine, he is entitled to that article, and should, manifestly, assure himself that he is getting the pure substance, and is not paying turpentine prices for petroleum products.

As to the use of the term "turpentine," as in the case of the "Chicago Turpentine," or "Norway Turpentine," this is a misnomer, these products not being turpentine in any sense of the word.

[1] *J. Soc. Chem. Ind.*, **16**, 519 (1897).

METHODS OF DETERMINATION.

Because of the comparatively low value of petroleum products as compared with pure turpentines, and because of their entire differences in chemical composition, as well as in physical properties, the determination of even trivial amounts of these substances is the principal problem in the examination of turpentines. The quantitative determination presents many difficulties, and chemists experience considerable trouble in deciding with certainty as to the presence or absence even of this form of adulteration.

As an example of hasty, incorrect, and almost amusing misinterpretation of analytical results, the following letter may be of interest. It came from a large user of turpentine in regard to a sample of wood turpentine, reported pure by us, and pronounced adulterated to the extent of 40 per cent. with petroleum oil, by their chemist:

"We wrote that we would report more fully to you on the sample of wood turpentine. Our chemist advises us as follows:

" 'Am sending you samples of the fractions separated in the distillation of the turpentine sample in question. Your attention is called to the low distillation points and gravities of Nos. 1 and 2, and also their objectionable odor. These portions do not exist in good turpentine. Number 3 and number 4 are too low in gravity, due to the presence of lighter oils, boiling at the same point as the turpentine. Nos. 5, 6, and 7 should not comprise over 5 per cent. of the sample, whereas in this sample they make up 42 per cent. You will notice the heavy, greasy character of No. 7. This certainly would not be a desirable turpentine sample.' "

"In explanation of the above we would say that Nos. 1 and 2 distilled at below 300° and comprised 7 per cent. of the sample. Nos. 3 and 4 distil at 302° to 340°, and the gravity is 0.850 of the first and 0.852 of the second. Nos. 5, 6, and 7 have a gravity between 0.852 and 0.930. No. 7, which comprises 5 per cent. of the sample we sent him, is a dark red, vile-smelling liquor. . . . . "

The above statements are tabulated below for the sake of convenience:

Fraction.	Nos. 1 and 2.	No. 3.	No. 4.	Nos. 5 and 6.	No. 7.
Per cent.....	7			37	5
Remarks.....	strong odor			should not be over 5%	dark; vile odor
Sp. Grav.....		0.850	0.852	0.852 to 0.930	
Boiling point.	below 150°	150° to	170°		

A comparison of these results with those given

in the table below will show that the chemist is making the erroneous assumption that the properties of turpentine and wood turpentine are identical, and these incorrect premises must necessarily lead to entirely incorrect conclusions.

The methods at present employed for detecting and determining petroleum products in turpentine are:

1. Fractionation with or without subsequent examination of the fractions by physical methods.

2. Polymerization with sulphuric acid and measurement of the residual oil.

3. Repeated polymerization with sulphuric acid and determination of the refractive index of residual oil.

4. Polymerization with nitric acid, and measurement of the residual oil.

Fractionation.—In carrying out this process the same details of procedure should always be employed, and the results compared with those on the same variety of turpentine of known purity. One variety of wood turpentine cannot be compared with another, nor either of them with pure gum turpentine.

F. W. Richardson and J. L. Bowen[1] recommend fractionation and determination of the refractive indices of the fractions; but any method based on physical measurements cannot be relied on for quantitative work because of the different physical constants for different petroleum products. In the article referred to, the refractive index of turpentine is given as 1.470 to 1.473, and of petroleum products as 1.41 to 1.46, which brings the minimum for the former, and the maximum for the latter entirely too close together.

A series of distillations of known mixtures, the boiling points of like fractions being noted, together with their readings in the butyro-refractometer, gave the following:

It is interesting to note that in the case of "kerosene adulterant," which is a petroleum product, chosen commercially for the purpose of adulterating turpentine, and of "elaine oil," a high-grade commercial kerosene, an addition of 5 per cent. cannot be recognized sharply. "Erco spirits," which is a lighter fraction, is easily detected qualitatively by this method. "Hexane," a very light petroleum ether, is not used for adulteration, but an addition of 5 per cent. can be readily recognized as above.

Altogether this method is not satisfactory. The products most frequently used may escape even qualitative detection, and the lighter products could be much more easily, and just as surely, found by a mere flash point determination.

Polymerization with Sulphuric Acid.—The method of shaking a measured quantity of the sample with concentrated sulphuric acid, and reading the residual oil after a given length of time, is used very largely by paint chemists. The method is dangerous, on account of possible explosions, the results at best very little better than a guess, especially if the adulterant is present in small quantities only.

The modification devised by McCandless[2] is quite ingenious, and fairly satisfactory in many cases. He treats a 100 cc. sample gradually with 50 cc. of concentrated sulphuric acid, shaking and cooling, repeats the process until a butyrorefractometer reading of 22 or less is reached, and then measures the surviving oil.

The method has, however, several drawbacks: the operation must be carried on repeatedly; the loss is considerable. Again, a petroleum fraction might be used having a refractometer reading greater than 22 and cause confusion, or escape detection, and a fraction heavy enough not to be carried over by steam, certainly would not be found.

	Wood pulp. B.P.-Rf.	Steam wood. B.P.-Rf.	Stump wood. B.P.-Rf.	Pure turp. B.P.-Rf.	5% kerosene. B.P.-Rf.	5% elaine. B.P.-Rf.	5% erco. B.P.-Rf.	5% hexane. B.P.-Rf.
Start.......	170 85	150 56	124 60	153 58	153 56	152 58	152 48	110 22
10 cc.......	171 85	156 57	150 68	155 58	155 56	153 58	154 53	150 49
20 cc.......	171 85	157 57	157 70	156 58	156 56	156 58	156 54	155 55
30 cc.......	171 86	157 57	161 70	156 58	157 57	156 58	157 55	157 57
40 cc.......	171 87	157 57	163 70	156 59	157 57	158 58	158 57	157 57
50 cc.......	171 87	157 57	168 70	156 59	157 57	158 58	158 57	157 57
60 cc.......	172 87	158 57	171 70	157 59	158 57	158 58	158 57	158 58
70 cc.......	172 88	160 57	174 71	158 60	158 57	159 58	161 57	158 58
80 cc.......	173 88	162 59	177 73	160 62	159 58	161 59	163 57	159 58
90 cc.......	175 90	167 60	183 79	162 65	162 59	165 59	167 58	160 60
Residue....	— 99	— 80	— 99	— 86	— 84	— 78	— 83	— 84
					of the adulterant		of the adulterant	
Sp. gr......	.8625	.8660	.8670	.8680	.7770		.7552	
Refract....	95	58	77	65	8	25	0	low
Solids......	0.6	1.2	3.5	1.0				

[1] *J. Soc. Chem. Ind.*, 27, 613.

[2] *J. Am. Ch. Soc.*, 26, 981.

Polymerization with Fuming Nitric Acid.—The method of Burton[1] cannot be recommended, being very dangerous, exceedingly trying and time-consuming and, at best, not at all accurate. His details, when tried experimentally, will be found to be quite impracticable for a laboratory method.

The modification, or rather the combination, of old methods, employed by the writer with entire success, is comparatively easy, is safe and rapid, includes all the possible fractions of petroleum products, and gives almost quantitative results, except in the case of very light naphtha, which, to the writer's knowledge, is never employed for purposes of adulteration. Even in this case as much as 50 per cent. of the amount present is readily separated, and as little as 1 per cent. of added ordinary mineral product may be determined with certainty.

The appended table shows laboratory results, obtained on various known substances and mixtures:

	Wood pulp.	Stump turp.	Pure turpentine.	1% kerosene.	5% kerosene.	5% hexane.	5% elaine.	5% heavy mineral oil.
Steam distil....	trace	4.5	0.3	1.0	1.0	1.0	4.5	9.0
Refractometer .		high	high	high	high	high	78	80
H_2SO_4 distil....	70	17	8.0	10.0	14.0	12.0	10.0	7
Refractometer .	100	90	77	60	48	63	50	90
HNO_3 treatm't.		none	0.5	1.5	4.5	3.0	5.0	5.0
Refractometer .			33	9	0.0	low	18	
Refractometer of the adulterant				8	8	low	25	60

The method in detail is as follows: 100 cc. sample, in a suitable flask (500 cc. Jena Kjeldahl answers nicely), is distilled in a current of live steam. The residue and distillate are transferred to separatory funnels and the water tapped off. The distillate is returned to the flask, treated with 500 cc. of concentrated sulphuric acid very gradually, shaken, and carefully cooled (McCandless's method). 25 cc. water are added and the mixture distilled with steam, to a total of 100 cc. With pure turpentines the amount of oil is uniformly 8 cc., an excess indicating adulteration. This oil is added to the residue from the first direct steam distillation.

A volume of fuming nitric acid, equal to three times that of the combined residues, is placed in a separatory funnel and *thoroughly cooled* in ice water. The combined oils are now added, drop by drop, shaking carefully and keeping cold. After all the oil has been added, allow to rest a few moments and draw off the acid layer. Wash the remaining oil once with fuming nitric acid, twice with ordinary strong nitric acid, and finally several times with water. Measure the volume.

1 *Am. Ch. J.*, **12**, 102.

The refractometer readings may advantageously be made on the various products obtained, but are by no means essential.

With pure turpentine a residuum of about 0.5 per cent. will be obtained, and allowance for this must always be made.

In the case of wood turpentine no such residuum is obtained, or at most, a mere trace, and no correction is necessary.

In the above series of experiments, then, the results, after making the correction, are:

	Added, per cent.	Found, per cent.
Kerosene adulterant..................	1.0	1.0
Kerosene adulterant..................	5.0	4.0
Elaine oil..........................	5.0	4.5
Mineral oil, heavy..................	5.0	4.5
Hexane..............................	5.0	2.5

showing that with such petroleum products as are commercially employed, the method yields almost quantitative results, irrespective of the physical constants thereof, or of the turpentine employed. As little as one per cent. is found without any trouble. With exceedingly light products—which are not used, however—the results would be low.

LABORATORY OF
MARINER AND HOSKINS,
CHICAGO.

THE DETERMINATION OF TOTAL, FIXED AND VOLATILE ACIDS IN WINES.

By JULIUS HORTVET.

Received September 21, 1908.

Considered from the standpoint not only of the food chemist but of the industrial chemist as well, determinations of total, fixed and volatile acids in wines are among the most important that are required in a complete course of analysis. These determinations are necessary not only for the judging of wines in accordance with legal standards of purity, but they also afford at times a very crucial insight into conditions relating to soundness or quality. At an earlier date than the latter part of the last century these considerations were not so much emphasized, doubtless because they were but little understood.

The first methods of analysis were of such a character as one might expect in the beginnings of our knowledge of fermented liquors as a class. The first known method of determining volatile acids

consisted in distilling a measured quantity of the sample to about one-third of its original volume and titrating the distillate. The results must obviously have been too low. The next step appears to have been in favor of an indirect course of procedure whereby the total acids were first titrated, then the wine evaporated off and the fixed acids titrated in the residue. From the difference between these titrations was calculated the amount of volatile acids. Various modifications of this method came into use.

Kissel[1] proposed evaporating the wine with sand or granulated glass, then drying the residue in an oven before titrating the fixed acids.

Weigert[2] evaporated 20 cc. of wine together with sand or pumice or paper cuttings in a small beaker, then heated the residue for a time at 100° C.

Nessler and Barth[3] evaporated 20 cc. of wine and heated the residue 20 minutes on a boiling water-bath.

In all these methods the aim appears to have been to liberate the total volatile acids by a prolonged heating of the extract. That an appreciable change might occur in the extract constituents as a result of such treatment was not at first conceived. At a later date, however, there developed grounds for the belief that certain of the fixed acids disappeared, in consequence of which, on titrating the residue, there was obtained too small a result. Hence the result for volatile acids would be too high. These considerations finally resulted in the abandonment of the so-called indirect methods, and it was again proposed to separate the volatile from the fixed acids by means of distillation and to titrate the volatile acids in the distillate. But because the volatile acids pass over only slowly and with difficulty, a simple distillation as in the determination of alcohol could obviously not be employed.

First Kissel[4] proposed a method which was substantially as follows:

Fifty cc. of wine were heated to boiling with 20 cc. of a solution of phosphoric acid of specific gravity 1.12, distilled from a retort on a sand-bath to 50 cc. distillate, 50 cc. of water added, the distillation continued to an additional 50 cc. distillate, and the operation repeated three times until a total of 250 cc. of distillate was obtained. This method was very laborious and slow, the determination requiring from four to six hours' time and constant close supervision.

[1] *Zeitschr. Analyt. Chemie*, **8**, 416 (1869).
[2] *Ibid.*, **18**, 208 (1879).
[3] *Ibid.*, **22**, 166 (1883).
[4] *Ibid.*, **8**, 416 (1869).

Weigert[1] distilled 50 cc. of wine to extract consistency under reduced pressure in a brine bath at 109° C., added 50 cc. of water and again distilled.

Later, Wolff[2] devised a method of distilling under diminished pressure on a sand-bath, allowing the wine and finally water to pass slowly through a funnel-tube into the flask.

Nessler and Barth[3] then came forward with a new method in which it was directed to distil 50 cc. of wine in a calcium chloride bath at 119° C. The distillation was prolonged for a time after the wine was reduced to a syrupy consistency and finally a stream of carbonic oxide gas was passed through the distilling flask.

Shortly afterwards, in 1883, Lindemann[4] described a method of driving out the volatile acids by steam, and this method forms the basis of the official methods which for some years have been prescribed in Europe and in America. In its essential details, the present official method[5] is as follows:

Fifty cc. of wine are distilled in a current of steam, in the meantime heating the flask containing the sample until the liquid boils and regulating the flame so that the volume remains constant. Two hundred cc. of distillate are collected and titrated with tenth-normal sodium hydroxide, using phenolphthalein as an indicator.

Chemists who have had considerable experience with this method must have noticed that it often happens that distillates collected beyond 200 cc. show a more or less strong acid reaction. This is the case especially with certain red wines, notably Burgundys, Ports and Clarets and wines of the Sauterne type. In fact, as the accompanying table shows, it seldom if ever occurs that the first 200 cc. distillate contains, even to a fair approximation, the total volatile acids. In some instances it is seen that by carrying the distillation beyond 200 cc. the error is very considerable. For example, following closely the official method and collecting 400 cc. of distillate, there are shown the following rates of increase in the total volatile acids: in a Burgundy, approximately 14 per cent.; in two samples of Port, respectively 13 and 14 per cent.; in a Claret, 13 per cent.; and in a white wine, 9 per

[1] *Zeitschr. Analyt. Chemie*, **18**, 208 (1879).
[2] *Repert. Analyt. Chemie*, **1**, 213 (1883).
[3] *Zeitschr. Analyt. Chemie*, **22**, 166 (1883).
[4] *Ibid.*, **22**, 516 (1883).
[5] Bull. 107, U. S. Dept. Agr., p. 86.

cent. There occur indeed wines in which the volatile acids appear never to become completely exhausted, in which, in fact, the distillate fails to appear permanently neutral even after very prolonged distilling. This phenomenon may be attributed not so much to acids of difficult volatility as to a possible decomposition of the extract constituents under the influence of prolonged heating by the direct action of the flame which the official directions require should be maintained below the flask containing the sample. It would seem, therefore, that 300 cc., or at most 400 cc., of distillate should contain practically all of the volatile acids, and that it may not be necessary or practical to prolong the distillation until the last portions of the distillate are neutral. The results obtained on the sixteen samples of wine included in the foregoing table show that in only four cases did the fifth 100 cc. of distillate require as much as 0.2 cc. of tenth-normal alkali to neutralize; hence, for practical purposes it may be assumed that the vanishing point of the volatile acids occurs when 500 cc. of distillate have passed over. On this basis, the results obtained show that the proportion of volatile acids collected in the first 300 cc. of distillate ranges from 90.0 to 95.7 per cent., only four samples showing a proportion slightly greater than 95 per cent. Thus, even in the present official method, if the entire apparatus be of fixed dimensions and relations in addition to the other conditions expressly stipulated, a large part of the fundamental error is still retained even by carrying the distillation to 300 cc. If the distillation be conducted slowly and the volume of the wine permitted to become too large, an insufficient amount of volatile acids will pass over; if the distillation be too rapid and the volume of the wine be permitted to diminish too much, there may occur an overheating and the amount of volatile acids will be too great. Finally, in order to obtain a fairly acceptable concordance in results, the distillation must be watched from beginning to end with the greatest care.

It has also been recognized that the agreement in results obtained by several distillations on a given sample fails to reach as high a degree as ought to be expected, even in approximately exact determinations. When the distillations are carried out to 400 cc., or even until the vanishing point of acidity is fairly reached, the results often fail to agree within reasonable limits. A difference in the results of the titrations amounting to from 0.3 to 0.5 cc. of the standard alkali has often been noted, and the differences are commonly far greater at the close of the 200 cc. period, amounting to 0.6 or 0.8 cc. in several instances.

VOLATILE ACIDS IN WINES.

(Results according to present official method.)

Sample.[1]	Distillates. Results in terms of cc. N/1 NaOH required to neutralize: First 100 cc.	Second 100 cc.	Third 100 cc.	Fourth 100 cc.	Fifth 100 cc.	First 200 cc.	First 300 cc.	First 400 cc.	Total 500 cc.	Per cent. acid in first 300 cc.
1 Claret	6.30	2 10	0 60	0 30	0.15	8 40	9 00	9.30	9.45	95.2
2 Zinfandel	5.80	1.70	0.50	0.25	0.15	7 50	8.00	8.25	8.40	95.2
3 Burgundy	9.25	3.65	1.25	0.55	0.20	12 90	14.15	14.70	14 90	95.0
4 Sherry	4.65	1 55	0 50	0.25	0.10	6.20	6.70	6.95	7.05	93.6
5 Sherry	5.60	2.20	1.10	0.70	0.30	7 80	8.90	9 60	9.90	90.0
6 Port	10.70	3.45	1.25	0 65	0.25	14.15	15.40	16.05	16.30	94.7
7 Port	5.45	2.00	0 70	0.35	0.15	7.45	8.15	8.50	8.65	94.2
8 Muscat	2.75	1.00	0.40	0.25	0.10	3 75	4.15	4.40	4.50	92.2
9 Hock	2.85	0.90	0.50	0.25	0 10	3.75	4.25	4.50	4.60	92.4
10 White wine	4.45	1.45	0 80	0.45	0 15	5.90	6.70	7.15	7.30	91.7
11 White wine	6.90	2 25	0.50	0.35	0.20	9.15	9.65	10 00	10 20	94 6
12 Port	2 15	0.80	0 35	0.20	0.00	2.95	3.30	3.50	3.50	94.3
13 Sherry	5.90	2.40	0 85	0 45	0.15	8.30	9.15	9 60	9 75	93.8
14 Claret	7 65	2.65	0.95	0.40	0.15	10.30	11.25	11 65	11.80	95.7
15 Angelica	4.70	1.65	0.60	0 30	0.10	6.35	6.95	7.25	7.35	94.5
16 Port	4.10	1 95	0.75	0 35	0.15	6 05	6.80	7.15	7 30	93.1

Briefly, then, the objections to the present official method are:

(1) The method is complicated, requiring rather elaborate apparatus and tiresome supervision.

(2) The prolonged heating of the wine by the direct action of the flame doubtless affects in some manner the constitution of the acid ingredients.

(3) The results do not to a sufficient extent represent the total volatile acids.

(4) The results are not reasonably concordant in the hands of different persons or even in the hands of a single individual.

Owing to these considerations, various chemists

[1] Samples 1 to 11 furnished by California Wine Association, 1906; samples 12 to 16 obtained from various sources.

have proposed the abandonment of the direct method of determining volatile acids in favor of an indirect course of procedure. After a prolonged examination of the relative merits of these general methods, Windisch[1] proposes the following:

Twenty-five cc. of wine are titrated in the usual manner for total acids, using litmus or litmus paper as indicator. Another 25 cc. portion is then evaporated on a water-bath in a porcelain dish to 3 to 5 cc., the residue dissolved in about 25 cc. of hot water, the liquor again evaporated to 3 to 5 cc., the residue again dissolved in about 25 cc. of hot water, and the liquor evaporated a third time to 3 to 5 cc. Finally, the residue is dissolved in hot water and the fixed acids titrated, using litmus as an indicator. The difference between the results of these titrations represents the volatile acids.

Guerin[2] has devised a method which contemplates getting rid of coloring matter. The determination is made as follows:

Ten cc. of wine (previously boiled a few minutes under a reflux condenser) are treated with 5 cc. of a ten per cent. solution of mercuric acetate, filtered from the precipitate and washed with cold water until the filtrate and washings equal 300 cc. The colorless liquid is treated with 10 cc. of a twenty per cent. solution of sodium-potassium tartrate and titrated with fourth-normal potassium hydroxide, using phenolphthalein as an indicator. A blank determination is made with water in place of wine, using the same quantities of reagents and titrating as before. The difference between the results corresponds to the total acids. Another 10 cc. portion is evaporated gently on a water-bath to a thin syrupy consistency, mixed with a little hot water and evaporated again. The residue is taken up with boiling water, cooled and clarified, and the fixed acids titrated and determined as in the method for total acids. The difference between this result and that obtained for total acids correspond to the amount of volatile acids.

Roos and Mestrezat[3] heat 20 cc. of wine under reduced pressure on a water-bath and distil off the volatile constituents until the contents of the flask have been reduced to 2 to 3 cc. Twenty cc. of water are then run in and the distillation continued, under reduced pressure, until the volume is reduced to 5 to 6 cc. A second addition of 20 cc. of water is made and the volume finally reduced to about 10 cc. The fixed acids are titrated in the residue, using tenth-normal sodium hydroxide together with phenolphthalein as an indicator.

[1] *Zeitschr. für Untersuchung der Nahrungs und Genussmittel*, **9**, 70 (1905).

[2] *Jour. Pharm. Chemie*, **25**, 491–2 (1907).

[3] *Bull. Assoc. Chim. Sucr.*, **25**, 41–9 (1907).

Other investigators have proposed various modifications of a method of carrying out the volatile acids by means of a current of steam.

Curtel[1] heats 25 cc. of wine and 25 cc. of water in a small flask on a water-bath, in the meantine passing steam through the liquor. The fixed acids are titrated in the residue.

Robin[2] proceeds in the following manner: The apparatus consists of a 60 cc. ordinary round flask and a 250 cc. Erlenmeyer flask, the latter of which is provided with a stopper in which is fitted a funnel together with a delivery tube which leads to near the bottom of the smaller flask. Ten cc. of wine are introduced into the smaller flask, the water in the Erlenmeyer heated to boiling and the steam passed through the wine from 40 to 45 minutes, in the meantime heating the smaller flask gently by means of a small flame. The Erlenmeyer is then raised until the delivery tube does not dip into the wine, the tube rinsed off with water, the liquor transferred to a beaker and the fixed acids titrated.

In these methods the total acids are titrated in a separate portion of the sample and the volatile acids determined by difference.

Sellier[3] has described a simple apparatus which consists of a small wide-neck flask into which is fitted a cylindrical-shaped flask. In the bottom of the latter flask is a small opening leading inward through a siphon-shaped tube bent back upon itself and terminating at a point close to the bottom. In making the determination, 50 to 60 cc. of distilled water are placed in the larger flask, the smaller flask fitted into the wide neck by means of a section of rubber tubing, 10 cc. of wine run in and the water heated to boiling. The steam passing through the wine carries out the volatile acids, in the meantime causing no appreciable change in the volume of the wine liquor. When the water is reduced to about 5 cc. the flame is removed and as the apparatus cools the remaining liquor is drawn into the larger flask. The inner flask is rinsed out with a little hot water, the two flasks disconnected, the liquor cooled and the fixed acids titrated.

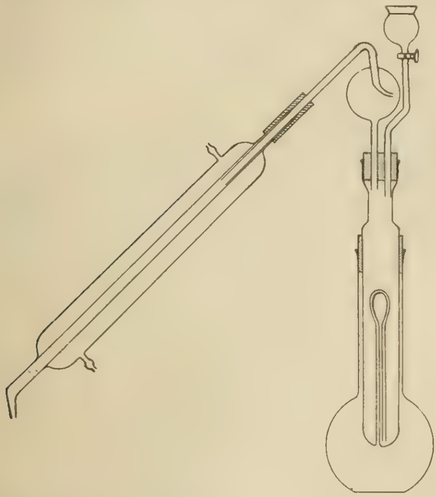
This method has been employed in this laboratory in the analysis of a number of samples of wine and in the investigation of a dozen or more of the common

[1] *Annal. Chim. Analyt.*, **6**, 361 (1901).

[2] *Jour. Pharm. Chim.*, **19**, 531–3 (1904).

[3] *Annal. Chim. Analyt.*, **6**, 414 (1901).

varieties of fruit juices, and has proven satisfactory not only from the standpoint of convenience in manipulation but on account of the fact that the results appear to be reliable and concordant. It has been considered, however, that the volatile acids are not collected but are allowed to dissipate into the air; hence it has occurred that while there is here afforded a simple, satisfactory means of separating the volatile from the fixed acids, it might also be desirable to condense the vapors and titrate the volatile acids in the distillate. By joining a condenser to the flask containing the sample there is provided an apparatus whereby may be



determined in one operation both the volatile and fixed acids on the same portion of wine.

The apparatus, as now constructed, consists of a 300 cc. spherical, flat-bottomed flask provided with an elongated wide neck. Into the neck of this flask is fitted a 75 cc. cylindrical-shaped flask provided with a siphon-like tube as in the apparatus of Sellier. Into the latter flask is fitted a small funnel with stop-cock and a delivery tube with safety bulb leading to a condenser. The distillate is received in a 100 cc. cylindrical graduate.

Volatile and fixed acids are determined as follows: One hundred cc. of recently boiled distilled water are poured into the larger flask, the smaller flask tightly fitted into the wide neck by means of a short section of rubber tubing, 10 cc. of wine (previously freed from carbonic acid gas) run in, the stop-cock closed and the water heated to boiling. Excessive foaming is prevented by adding to the wine a small piece of paraffin. When 50 cc. of distillate have passed over, the graduate is emptied into a beaker and the distillation continued. The distillate is titrated with tenth-normal sodium hydroxide, using phenolphthalein as indicator. The distillation is stopped when an additional 10 cc. of distillate requires not more than one drop of the standard alkali solution to neutralize. Usually 80 cc. of the distillate will include practically all of the volatile acids. On cooling the apparatus, the wine liquor is siphoned into the lower flask. The remaining liquor is rinsed out by running a small amount of hot water through the funnel tube and the two flasks disconnected. In the case of a white wine or a light colored wine, 100 to 200 cc. of boiled distilled water are added and the fixed acids are titrated with tenth-normal sodium hydroxide, using phenolphthalein as an indicator. In the case of a highly colored wine, the liquor is cooled, made up to 100 cc., 25 cc. measured out and diluted with boiled distilled water and titrated as before.

In order to prepare a wine for analysis, various methods have been proposed. The one commonly given directs that the sample be thoroughly shaken or poured for a short time from one vessel to another and filtered. Such a method may suffice with wines having a very low gaseous content, but with wines fermented under pressure and with carbonated liquors especially a more effective method should be required. Some analysts heat the sample in an open dish to incipient boiling, while others subject the wine to boiling under a reflux condenser. The latter method is given by Breteau[1] in connection with the determination of total acids, as follows:

Ten cc. of wine are measured into a 300 cc. flask, 200 cc. of distilled water added and the liquor boiled 3 minutes under a reflux condenser. After cooling, two drops of phenolphthalein are added and the solution titrated with decinormal sodium hydroxide. In the same manner, 210 cc. of distilled water are titrated and the total acids calculated from the difference between the results of the two titrations.

In the laboratory of the California Wine Association the following method[2] is employed:

Ten cc. of wine are measured into a 500 cc. beaker, without the addition of water. The wine is well shaken to remove carbon dioxide and titrated directly with fifth-normal sodium hydroxide. In

[1] Guide Partique des Falsifications et Alterations des Substances Alimentaires, par Pierre Breteau, p. 318.

[2] From letter received from C. S. Ash, Chemist of Cal. Wine Assoc.

the case of a heavy colored wine no indicator is used, the coloring matter serving to indicate the end-point of the titration. In the case of a white wine, the same method of procedure is followed excepting that a little neutral litmus is added. In titrating light colored wines, it may at times be advisable to add litmus but the indicator is not added unless absolutely required.

A comparison of results obtained by various methods of determining total, fixed and volatile acids in wines is shown in the accompanying table. Total acids were determined by the California Wine Association method, by the method of Windisch and by the proposed new method based on that given by Breteau. Previous boiling was omitted in the case of samples which appeared to be practically free from carbon dioxide. Fixed acids were determined by the method of Windisch, by the method of Sellier and by the proposed new method of titrating the liquor remaining after driving off the volatile acids by means of steam distillation. Volatile acids were determined by the indirect method of Windisch and by the proposed new direct method of titrating the acids collected in the distillate. In the Windisch methods the titrations were made using litmus paper as an indicator and in the method of Sellier, as in the proposed new methods, phenolphthalein was used. Results are expressed as the number of cc. of normal total, fixed and volatile acids respectively in 100 cc. of the wine.

The results obtained by the California Wine Association method do not appear to be satisfactory or to bear any relationship to the results obtained by either of the other methods. In the Angelicas, Ports and Sherrys, chiefly, much difficulty was experienced in carrying out the titrations, and the results were scarcely more satisfactory when litmus tincture was used. Not only were the successive color changes which occurred during the addition of the alkali not uniform among the different samples, but the final change, at what was usually with great difficulty judged to be the end-point of the titration, varied greatly with the character of the wine. In titrating by the Windisch methods, the point of neutrality was judged to be attained when a small drop of the liquor placed on delicate blue litmus paper just ceased to produce a perceptible red. There appeared to be decided disadvantages in the use of litmus paper and the use of litmus solution, even in a clear distillate, is open to a serious objection which will be stated presently. In colored wines, especially, the difficulties were very great, and it was found well-nigh impossible at times to devise a means whereby to judge with reasonable certainty the true end-point of the titration. It was found, however, after considerable practice, that fairly concordant results were obtainable by this method in the majority of instances. Phenolphthalein, on the other hand, while not entirely unobjectionable, was found to give far greater satisfaction. While it was not always convenient to titrate on the undiluted sample, especially in the case of wines containing more or less natural coloring matter, it was found to be entirely permissible, as in the titration of cider

RESULTS FOR TOTAL, FIXED AND VOLATILE ACIDS IN WINES.

(Results expressed as cc. N/1, acid in 100 cc. of sample.)

	Total acids				Fixed acids.					Volatile acids				Vol.: fixed acids.	
							Proposed new method.				Proposed new method.				
Samples.[1]	Method of Cal. Wine Ass'n.	Method of Windisch.	Proposed new method.	Calculated from fixed and vol. acids.	Method of Windisch.	Method of Sellier.	Using litmus.	Using phenolphthalein.	Calculated from total and volatile acids.	Method of Windisch.	Using litmus.	Using phenolphthalein.	Calculated from total and fixed acids.	By method of Windisch.	By proposed new method.
1 Angelica...	4.30	4.16	5.80	5.80	3 32	4.90	3.40	5.00	5.00	0.84	0.70	0 80	0.80	1: 3.95	1: 6.25
2 Claret.....	7.70	7.52	9.60	9.55	6.80	8.00	7.00	8.00	8.05	1.72	1.40	1.55	1.60	1: 3.95	1: 5.16
3 Port.......	5.20	5 60	7.20	7.15	4 36	5.90	5.00	6.00	6.05	1.24	0.95	1.15	1.20	1: 3.51	1: 5.21
4 Riesling...	6.00	6.36	7.45	7.50	4.80	6.15	5.20	6.10	6.05	1.56	1.15	1.40	1.35	1: 3.07	1: 4.35
5 Sherry	4.00	4.50	5.35	5 35	2.96	3.95	3.00	3.90	3.90	1.54	1.20	1.45	1.45	1: 1.92	1: 2 69
6 Zinfandel ..	8.70	7.92	9.70	9.75	6.14	8.20	6.55	8.10	8.05	1.78	1.40	1.65	1.60	1: 3.44	1: 5.06
7 Sauterne...	6.70	7.58	8.55	8.60	5.64	6.75	5.50	6.75	6.70	1.94	1.30	1.85	1.80	1: 2.90	1: 3.69
8 Sauterne...	7.10	8.16	9.15	9.20	5.48	6.40	5.00	6.50	6.45	2.68	2.10	2.70	2.65	1: 2.04	1: 2.40
9 Sauterne...	7.70	8 20	8.90	8 95	6 00	7.30	6.00	6.95	6.90	2.20	1.70	2.00	1 95	1: 2.73	1: 3.47
10 Port.......	8.90	8.44	9.55	9.60	6.00	7.75	6.50	7.30	7.25	2.44	2.00	2.30	2.25	1: 2.46	1: 3.17
11 Sherry.....	5.50	5.80	6.60	6.60	3.60	4.80	3.70	4.40	4.40	2.20	1.90	2.20	2.20	1: 1.64	1: 2.00
12 Claret.....	5.60	10.60	11.90	11.90	7.40	9.60	8.20	9.20	9.20	3.20	2.40	2.70	2.70	1: 2.31	1: 3.41
13 Port.......	6.80	6.30	7.10	7.10	4.40	5.50	4.50	5.20	5.20	1.90	1.60	1.90	1.90	1: 2.32	1: 2.74
14 Sherry.....	5.90	6.40	7.20	7.25	3.60	5.70	4.00	4.80	4.75	2.80	2.00	2.45	2.40	1: 1.28	1: 1.96
15 Claret.....	8.50	8.40	9.50	9.60	6.20	7.90	6.40	7.70	7.60	2.20	1.60	1.90	1.80	1: 2.82	1: 4.05

[1] Samples 1 to 6 furnished by California Wine Association, 1908, samples 7 and 8 obtained from local dealers, samples 9 to 12 furnished by Irondequoit Wine Co., 1908; samples 13 to 15 furnished by Garrett & Co., 1908.

vinegars, to dilute with boiled distilled water in order to carry out a satisfactory titration with phenolphthalein. It has been shown that the end-point of a titration can be very accurately judged, even in a deeply colored wine, and that the addition of water to the extent of from 100 to 200 cc. to 10 cc. of sample does not introduce a serious error in the result. As in a cider vinegar, the change in the color of a wine occurs at a much earlier stage than the change in the phenolphthalein and there is no difficulty in detecting distinctly the change in the indicator.

As already pointed out, the results shown in the first column of figures are at best only fair approximations. In the majority of instances, it was observed that when litmus paper was used the titrations were carried somewhat beyond the point of neutrality which seemed to be indicated by the change in the natural coloring matter of the wine. It is also noted that results obtained by titrations employing litmus are uniformly much lower than results obtained with phenolphthalein. This is true not only in the titrations of total and fixed acids but also in the direct titrations of the volatile acids. In comparison with the results obtained proper indicator for wines and fruit products in general. Litmus is not recommended for titrating such acids as tartaric, acetic, tannic, succinic and malic. In titrating tartaric acid with litmus as indicator, the change is gradual and the end-point indistinct, while in titrating acetic acid the acetate of sodium formed is alkaline to litmus and tends strongly to hasten the end-point. Similar results are obtained on titrating solutions of succinic and malic acids. In a solution of tannic acid containing litmus the change in the color of the indicator takes place almost immediately after beginning the titration and only a small proportion of the actual acid is indicated. Phenolphthalein, on the other hand, is a very satisfactory indicator with all these acids. Acetate of sodium is neutral to phenolphthalein and the theoretical amount of acetic acid is obtained. In the case of tannic acid, the end-point is good, about 80 per cent. of the acid being shown. The total acid is obtained after boiling a short time with a measured small amount of tenth-normal hydrochloric acid. As a means of shedding some light on the differences occurring in titrating wines with these two indicators, the determinations shown in the following table have been carried out:

Comparison of Litmus and Phenolphthalein as Indicators in Titrating Some of the Organic Acids Existing in Wines.

			cc. N/1 acid in 100 cc.			Per cent. acid indicated.	
Acids.	Description.	Grams in 100 cc.	Calculated	Using phenolphthalein.	Using litmus.	Using phenolphthalein.	Using litmus.
Tartaric	Eimer & Amend, pure	0.4000	5.33	5 35	5 10	100 3	95.6
Acetic	Mallinckrodt's 99 per cent	0 4040	6.67	6 70	6.35	100.4	95.2
Potassium bitartrate	Eimer & Amend, pure	0.4000	2.12	2.10	1.90	99.0	89.6
Tannic	J. T. Baker Chemical Company's pure	0.5000	2.79	2.20	0.40	78.8	14.3
After boiling with dilute HCl				2.80	0.40	100.3	14.3
Average per cent. total acids indicated						94.4	73.6
Average per cent acids indicated (omitting acetic)						92.6	66.5

with phenolphthalein, litmus indicates approximately from 77 to 92 per cent. of the total acids and from 58 to 85 per cent. of the fixed acids. Doubtless there are theoretical reasons underlying these differences, and the question may well be raised as to whether chemists have given sufficient attention to theoretical considerations in choosing indicators to be used in titrating the acids in wines. In the first place, there can be no justification for the selection of the natural coloring matter of a wine as a correct indicator in titrating either total or fixed acids. Enough is known regarding the action of the oenocyanin and other natural coloring matters of wines in the presence of acids and alkalies to exclude such substances as suitable for use as indicators. In the case of litmus, also, there are important reasons which should bar it as a

In the table headed Results for Total, Fixed and Volatile Acids in Wines, the results shown in the tenth column of figures are somewhat higher than the results shown in column twelve. Such discrepancies, however, lose their significance when it is considered that, in the determination of volatile acids by the indirect method, not only are the results of titrations using litmus as indicator incorrect, but the titrations of total and fixed acids are not made under comparable conditions. While it is unquestionably true that the volatile acids may be driven off by repeated evaporation in an open dish, it does not follow that the results obtained by means of the two titrations can be correct. It is conceivable that important changes may occur during the prolonged heating of the wine in order to reduce the material for a third time to a pasty

consistency; at any rate, we have no positive knowledge that the so-called fixed acids occurring in the final residue represent the actual fixed acids in the original wine. A titration of the residue may suffice as an indication of the acids present after driving off the volatile constituents by the prolonged heating, but to employ the result of such a titration as a factor in the calculation of the actual volatile acids appears to be an unwarrantable proceeding.

In expressing the results of analysis, the orthodox custom appears to be to calculate the fixed and total acids as tartaric and the volatile acids as acetic. It is impossible to concede any advantages in favor of this custom. It may be safe to assume that in wines the fixed acids are in the main tartaric and the volatile acids acetic; but, even on such assumptions, the results are strictly erroneous and not readily comprehensible. Such a method applied to the various fruit juices and ciders would fail to give significant results in practically all cases, and the case is still worse when one undertakes to apply the method of calculating the acids as sulphuric. Instead of these conventional methods, it has been found better to adopt the plan of expressing all results for total, fixed and volatile acids in terms of the number of cc. of normal acid in a definite measure, say 100 cc., of wine. There will then be afforded results which can be readily compared and comprehended. Furthermore, in case it be required to calculate results in terms of any particular acid, such an operation can easily be carried out.

Chemical Laboratory,
Minnesota State Dairy and Food Department,
St. Paul, Minnesota.

[Contribution from the Department of Food and Drug Inspection of the Massachusetts State Board of Health.]

A COMPARISON OF METHODS FOR THE PREPARATION OF MILK SERUM.

By Hermann C. Lythgoe and Lewis I. Nurenberg.

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It is a well-known fact that milk serum is of more uniform composition than milk, consequently its constants, particularly the specific gravity have been used for many years for the detection of added water. Recently the index of refraction has been suggested for this purpose and was first employed by Villiers and Bertault[1] in 1898 who prepared the serum by placing a mixture of two volumes of 1 per cent. acetic acid and one volume of milk in a flask connected with a reflux condenser, heating to the boiling point, cooling and filtering. The serum was examined in the oleo-refractometer of Amagat and Jean. Matthes and Müller[1] in 1903 first suggested the use of the Zeiss immersion refractometer for this purpose, using the serum obtained from spontaneously soured milk. Leach and Lythgoe[2] in 1904 prepared the serum according to the method of Woodman[3] with 25 per cent. acetic acid, taking the refraction with the immersion refractometer. Baier and Neumann[4] mixed the milk with an asaprol citric acid solution in the cold, filtered, and determined the index of refraction of the filtrate with the Wollny milk fat refractometer. Ackerman[5] heated the milk with a calcium chloride solution and determined the index of refraction of the serum by means of the immersion refractometer.

[1] *Bull. Soc. Chim.*, **19**, 305.

During the past two years many samples of milk of known purity have been examined in the laboratory of food and drug inspection of the Mass. State Board of Health to which two or more of the above methods have been applied. The specific gravities of the sera were obtained at 15°, and the indexes of refraction on the immersion refractometer at 20°, and the results are reported in the accompanying tables. The samples of milk were all milked in the presence of an inspector or an analyst of this department.

The details of the methods used for the preparation of the milk sera are as follows:

Acetic Acid Method.—To 100 cc. of milk at about 20° C. add 2 cc. of 25 per cent. acetic acid, mix well and place in a water bath at 70° C. for 20 minutes. Cool 10 minutes in ice water and filter.

Natural Souring Method.—Allow the samples to sour spontaneously and filter off the serum.

Calcium Chloride Method.—The details have been slightly modified from the method of Ackerman indicated above. Place 90 cc. of milk in a flask, add 0.75 cc. of calcium chloride solution, sp. gr. 1.1375 (when diluted 1 : 10 this solution reads 26 on the immersion refractometer at 17.6° C.), shake thoroughly, close the flask with a cork carrying a glass tube to act as a reflux condenser, place in a boiling water bath for 20 minutes, cool to 20°, mix the condensed water and serum without shaking, and filter.

[1] *Zeit. offentl. Chem.*, **10**, 173.
[2] *J. Am. Chem. Soc.*, **26**, 1195.
[3] *Ibid.*, **21**, 503.
[4] *Zeit. Nahr-Genussm.*, **13**, 369.
[5] *Ibid.*, **14**, 186.

Asaprol Method.—The precipitating solution is made by dissolving 30 grams of asaprol and 55.8 grams of crystallized citric acid in 1 liter of water. If the refraction is not 36.3 at 20° C. on the scale of the immersion refractometer add citric acid or water to make it so. Mix equal volumes of the above solution and the milk, shake well and filter.

TABLE I.

REFRACTION OF MILK SERA FROM KNOWN PURITY MILK.

Individual Cows.

Method.			
Acetic acid.	Natural souring.	Calcium chloride.	Asaprol.
46.2	47.7	..	..
45.9	44.6	..	38.4
45.8	44.0	..	..
45.7	43.4	40.1	37.0
45.6	43.5	..	..
45.5	41.5	38.7	37.1
45.1	41.5	39.0	36.8
44.9	41.5	39.8	36.1
44.8	43.8	..	..
44.8	43.7	39.2	36.0
44.7	43.5	..	36.6
44.6	..	38.5	36.6
44.5	45.0	..	..
44.3	42.8	..	35.7
44.4	43.8	..	36.7
44.3	43.0	..	..
44.3	42.8	..	..
44.3	42.3	39.0	37.0
44.2	41.2	38.6	37.0
44.2	41.0	..	..
44.1	43.0	39.1	36.7
44.1	40.7	38.2	36.8
44.0	42.2	38.7	..
43.9	44.5	..	..
43.9	42.6	..	..
43.8	44.0	..	..
43.8	44.0	..	..
43.8	43.0	..	36.7
43.8	41.6	..	..
43.7	44.2	..	37.5
43.7	42.6	..	..
43.7	42.4	..	..
43.7	41.5	..	36.9
43.6	43.0	..	..
43.6	43.0	40.0	36.3
43.6	42.0	38.6	36.3
43.5	43.5	..	..
43.5	42.8	..	..
43.5	41.0	38.4	36.3
43.4	43.1	..	..
43.2	43.3	..	..
43.2	42.2	..	..
43.2	41.8	38.9	36.6
43.2	40.9	..	37.4
43.0	43.7	..	..
43.0	43.2	..	..
43.0	42.8	..	..
43.0	42.3	..	..
43.0	42.0	..	..
43.0	41.7	..	..
43.0	41.5	..	..
43.0	41.4	39.1	36.4
43.0	41.1	38.4	36.6
43.0	40.9	..	..
42.9	43.6	..	36.5
42.9	43.0	..	..
42.9	41.4	39.0	36.7
42.8	..	..	37.4
42.7	..	38.8	..
42.7	..	38.0	..

TABLE I—(*Continued*).

Method.			
Acetic acid.	Natural souring.	Calcium chloride.	Asaprol.
42.6	41.3	38.1	36.1
42.5	42.2	39.3	36.3
42.5	41.5	..	..
42.5	..	38.2	36.6
42.4	43.3	..	36.4
42.3	43.7	39.0	37.0
42.3	41.9	..	36.8
42.3	41.6	39.8	36.6
42.3	40.8	38.8	36.7
42.2	42.0	..	37.0
42.2	41.0	.	..
42.1	44.0	..	36.8
42.1	43.7	..	36.6
42.0	41.0	..	..
42.0	40.3	37.1	36.2
42.0	40.2	36.8	35.8
41.8	40.5	..	..
41.7	40.9	38.2	36.1
41.7	..	38.0	..
41.7	40.0	36.8	36.2
41.6	43.9	..	36.0
41.5	40.4	36.4	35.7
41.4	40.3	38.4	35.6
41.3	40.3	..	..
41.2	40.0	..	..
40.6	40.7	36.6	35.8
40.5	39.3	..	..
40.4	38.3	..	..
40.0	40.1	..	..
Mixed Milk of Known Purity.			
43.6	42.9	39.0	37.5
43.5	42.0	38.7	..
43.4	40.8	38.2	36.7
42.5	41.0	39.4	36.3
42.1	41.3	..	..

TABLE II.

SPECIFIC GRAVITY OF MILK SERA FROM KNOWN PURITY MILK.

Individual Cows.

Method.			
Acetic acid.	Natural souring.	Calcium chloride.	Asaprol.
1.0333	....	....	1.0259
1.0330	1.0324	....	....
1.0329	1.0291	....	....
1.0327	1.0297	1.0275	1.0256
1.0324	1.0263	1.0274	1.0251
1.0323	1.0295	1.0276	1.0253
1.0322	1.0278	1.0272	1.0253
1.0322	1.0272	1.0274	1.0252
1.0320	1.0290	....	....
1.0319	1.0284	1.0270	1.0251
1.0318	....	....	1.0245
1.0318	1.0290	....	1.0254
1.0318	1.0260	....	....
1.0318	1.0273	1.0264	1.0252
1.0316	1.0275	1.0263	1.0253
1.0316	1.0300	....	1.0256
1.0316	1.0292	....	1.0252
1.0316	1.0300	....	....
1.0314	1.0281	1.0267	1.0252
1.0314	1.0306	....	....
1.0313	1.0276	1.0274	1.0251
1.0313	1.0282	1.0265	....
1.0312	1.0287	1.0268	1.0252
1.0312	1.0280	1.0269	1.0249
1.0312	1.0272	....	1.0250
1.0312	1.0282	1.0268	1.0252
1.0312	1.0285	1.0264	1.0244
1.0312	1.0295	....	....
1.0311	1.0235	1.0264	1.0250
1.0311	1.0272	1.0259	1.0249
1.0310	1.0277	1.0274	1.0248
1.0310	1.0236	....	....

TABLE II—(*Continued*).

Method			
Acetic acid	Natural souring.	Calcium chloride.	Asaprol.
1.0310	1.0275	....	....
1.0310	1.0270	....	....
1.0310	1.0284	.	....
1.0309	1.0270	1.0265	....
1.0309	1.0310	..	1.0244
1.0308	1.0290	. .	1.0247
1.0308	1.0295	....	1.0247
1.0308	....	...	1.0253
1.0308	1.0272	...	...
1.0307	1.0248	1.0270	1.0252
1.0307	1.0267	1.0274	1.0248
1.0307	1.0278	....	....
1.0306	....	...	1.0248
1.0306	1.0295	....	1.0256
1.0306	1.0304	....	....
1.0305	1.0292	....	....
1.0305	1.0306	....	....
1.0305	1.0274	1.0259	1.0245
1.0304	....	....	1.0245
1.0304	1.0285	....	....
1.0304	1.0270	....	....
1.0303	1.0260	1.0266	1.0252
1.0303	1.0294	...	....
1.0302	1.0265	1.0261	1.0247
1.0302	1.0282	1.0271	1.0249
1.0302	1.0290	1.0285	1.0243
1.0302	1.0285	....	1.0246
1.0302	1.0255	...	....
1.0302	1.0273	1.0256	1.0247
1.0301	1.0292	....	....
1.0301	1.0272	1.0258	1.0245
1.0301	1.0206	1.0264	....
1.0300	1.0290	1.0263	1.0245
1.0300	1.0293	....	1.0246
1.0300	1.0280	....	1.0245
1.0300	1.0293	....	....
1.0300	1.0264	...	....
1.0299	1.0280	....	1.0242
1.0299	1.0283	....	....
1.0299	1.0296	....	....
1.0298	1.0229	1.0258	1.0246
1.0298	1.0255	....	....
1.0298	1.0260	....	....
1.0298	1.0285	....	....
1.0298	1.0306	...	....
1.0296	1.0266	....	....
1.0296	1.0279	....	....
1.0296	1.0282	...	....
1.0296	1.0253	1.0259	....
1.0295	1.0264	....	....
1.0295	1.0279	....	....
1.0295	1.0306	...	....
1.0294	1.0274	...	....
1.0293	1.0282	....	....
1.0293	1.0223	1.0258	....
1.0292	1.0290	....	1.0235
1.0292	1.0285	....	....
1.0292	1.0270	1.0248	1.0244
1.0291	1.0276	....	....
1.0290	1.0236	1.0268	1.0238
1.0290	1.0264	....	....
1.0290	1.0268	1.0244	1.0240
1.0289	1.0261	1.0252	1.0239
1.0288	1.0221	1.0248	1.0241
1.0287	1.0307	....	....
1.0282	1.0249	...	....
1.0280	1.0350	...	....
1.0280	1.0254	....	1.0237
1.0280	1.0272	....	....
1.0280	1.0262	1.0234	1.0241
1.0274	1.0266	....	....
Mixed Milk of Known Purity.			
1.0312	1.0292	1.0264	..
1.0310	1.0284	....	..

TABLE II—(*Continued*).

Method.			
Acetic acid.	Natural souring	Calcium chloride.	Asaprol.
1.0308	....	1.0266	....
1.0306	1.0283	1.0258	1.0251
1.0302	....	....	1.0249
1.0300	1.0284	....	....

Of the above methods, the asaprol method is the easiest of manipulation, gives the clearest serum in the least time and shows the lowest refraction with the least variation. Unfortunately pure asaprol is very difficult to obtain and owing to the fact that it decomposes readily, it is not an easy matter to prepare different solutions that will give identical sera with the same sample of milk.

The calcium chloride method is the most difficult of manipulation and is liable to give a cloudy serum rather troublesome to read but the figures do not vary so much and are lower than those obtained by the acetic acid method. The natural souring method is too slow for ordinary use, but is valuable in the hot weather if the milk is nearly sour by the time it reaches the analyst. As a rule, the figures are lower than those obtained by the acetic acid method, but in a few cases they run higher. Four years' experience with the acetic acid method has shown it to be reliable, easy of manipulation, and to give concordant results. It is still used in this laboratory for the detection of added water in milk.

LABORATORY OF FOOD AND DRUG INSPECTION, MASSACHUSETTS
STATE BOARD OF HEALTH,
BOSTON, MASS.

NOTES.

ON THE USE OF INCANDESCENT LAMPS WITH VOLATILE SOLVENTS.

For the extraction with, and distillation of, volatile solvents the ordinary 8- and 16-candle power incandescent lamps may be employed to advantage as a source of heat. The 8-candle power lamp has been found to be more satisfactory for (ether) extraction, and the 16- for distillation. The lamp as used is enclosed in a slightly tapering cone, or cylinder of asbestos paper. By placing asbestos paper around lower part of extraction apparatus the flow of condensed solvent is easily regulated, and once regulated requires no further attention. Asbestos paper will also be found useful if placed around flask during distillation. Incandescent lamps may also be used to advantage for evaporation at low temperatures, especially when inflammable vapors are given off, the temperature being regulated by raising or lowering the source of heat.

The use of electricity for boiling the solvent during extraction gives a compact apparatus, everything being on

one stand; there is no danger from explosion due to flame; a steady, continuous source of heat, not affected by draughts or other external influences, is secured. The lamp socket is easily held in position by means of a clamp; the heat is instantly available, and quickly removed. Using this source of heat (ether) extractions are carried on continuously through the night, no attention being required after first regulating the flow of condensed solvent.

E. O. THOMAS.

THE BUREAU OF STANDARDS' ANALYZED SAMPLES.

It will be of interest to those of our readers who are not already informed to know that the Bureau of Standards is prepared to supply analyzed samples (150 grams each) of standard irons and steels, at the following rates:

Single samples of 150 grams, each sample.........	$2.00
In lots of three to nine samples, each sample......	1.67
In lots of ten to nineteen samples, each sample....	1.50
In lots of twenty samples or more, each sample....	1.25

Orders for samples should be accompanied by a remittance.

The list follows:

Cast Iron C with medium Si, P, Mn.
Cast Iron D with high Si, P, Mn.
Bessemer Steels with approximately 0.1, 0.2 and 0.4% C.
Basic Open Hearth Steels with 0.1, 0.2, 0.4, 0.6, 0.8 and 1% C.
Acid Open Hearth Steels with 0.1 and 0.2% C.

Cast Iron B is exhausted but will be replaced in time.

Bessemer bars with 0.6 and 0.8 per cent. C and acid open hearth bars with 0.4, 0.6, 0.8 and 1 per cent. C are on hand, but the process of preparing samples is very slow and it may be a year before the last of them is ready for distribution.

The preparation of special steel standards is under consideration.

It may be added that the Bureau is also prepared to distribute to applicants samples of an analyzed argillaceous limestone[1] suitable for the manufacture of Portland cement.

Samples of cane sugar of known calorific value for the standardization of calorimeters are also furnished by the Bureau. It is hoped to furnish in time a variety of materials for calorimetry, and also a very pure sugar for the standardization of polarimeters.

Announcement will be made in these columns whenever any standard samples are ready for distribution.

The Bureau also calibrates volumetric apparatus, for a small charge, provided the pieces have identification marks and conform in other respects to the Bureau's requirements. Circular No. 9, which may be had upon request, gives information in regard to these points.

W. F. HILLEBRAND.

[1] *Jour. Am. Chem. Soc.*, **28**, 229.

REPORT OF THE COMMITTEE ON THE ANALYSIS OF PHOSPHATE ROCK.

The first report of the committee appointed by the National Fertilizer Association on the analysis of phosphate rock has just been issued. The committee which was appointed early in the year by the Association consisted of Messrs. C. F. Hagedorn, C. H. Dempwolf, Jr., and F. B. Carpenter, all well-known chemists connected with large fertilizer interests. The essential features of the report, with the exception of the names of the analysts, follow:

To the Members of the National Fertilizer Association:

The discrepancies between the results of chemists in the analysis of phosphate rock have often been the cause of disputes between buyer and seller, sometimes resulting in costly litigation, and usually ending in a feeling of diminished confidence by the manufacturer for his chemist. While it is true that there are limits to the accuracy of analytical methods, we believed that the great variations were due mainly to the use of different methods or to various modifications of the same method. It was, therefore, considered to be of great importance that some work be done on this subject, and it was the object of this investigation to examine the various analytical methods for phosphate rock, which are now in use, with a view to the adoption by our Association of methods which will yield uniform results

Four sets of samples of the following kinds of phosphate rock were prepared: Tennessee Brown, Tennessee Blue, South Carolina and Florida. These were distributed among the chemists of our Association and the commercial chemists who make a specialty of fertilizer analyses. Each chemist was instructed to determine moisture, phosphoric acid (also calculated to calcium phosphate) and iron and aluminum oxides, using the routine method of his laboratory and to return a complete report of the results, together with a copy of his methods.

Thirty-one reports were received, which we have classified according to methods, giving in each case a brief outline of the method. Below each table we have also noted the important modifications of these methods.

MOISTURE.

We include in this table the essential points in the method in each case; *viz.*, the size of sample, time of drying and temperature of oven.

Analyst.	No. 1 Tenn. brown.	No. 2 Tenn. blue.	No. 3 Fla. pebble.	No. 4 S. C.	Weight, grams.	Time, hours.	Temperature C.
1	1.26	0.68	0.80	0.48	2	5	100
2	0.89	0.39	0.40	0.20	1	5	100
3	0.79	0.25	0.27	0.06	2	5	100
4	0.69	0.33	0.28	0.13	2	5	100
5	0.99	0.45	0.47	0.26	5	C.W.	100
6	0.92	0.43	0.48	0.30	5	5	100
7	1.06	0.45	0.54	0.27	2	5	100
8	1.10	0.50	0.45	0.25	2	5	100
9	1.14	0.52	0.66	0.34	5	5	105
10	1.09	0.42	0.46	0.20	2	4	100
11	1.16	0.55	0.66	0.38	10	5	100
12	1.14	0.55	0.66	0.55	2	2	100
13	1.22	0.54	0.62	0.34	20	12	100
14	0.93	0.38	0.52	0.26	....	...	...
15	1.37	0.72	0.87	0.50	10	C.W.	100–05
16	1.00	0.35	0.59	0.28	5	5	100
17	1.30	0.70	0.80	0.40	10 & 5	3	100
18	1.40	0.60	0.80	0.60	10 & 5	3	100
19	1.09	0.49	0.52	0.28	5	4	100
20	1.15	0.48	0.49	0.32	1	5	100
21	1.09	0.51	0.63	0.27	10	C.W.	105–10
22	1.06	0.53	0.63	0.40	5	5	100
23	0.57[1]	0.35	0.27	0.17	5	5	105–10
24	1.07	0.48	0.52	0.27	5	5	105
25	1.20	0.48	0.60	0.40	...	5	100
26	1.20	0.50	0.60	0.30	2	3	105
27	1.12	0.46	0.56	0.31	5	5	100

[1] Omitted from average.

Analyst.	No. 1 Tenn. brown.	No. 2 Tenn blue.	No. 3 Fla. pebble.	No. 4 S. C.	Weight, grams.	Time, hours.	Temperature C.
28	0.95	0.27	0.43	0.14	....	5	105
29	0.36[1]	0.35	0.35	0.23	2	5	100
30	1.02	0.46	0.52	0.27	5	5	100
31	1.50	0.73	0.84	0.48	5	C.W.	105
32	1.09	0.37	0.52	0.24	2	2	100
Average	1.10	0.48	0.56	0.31			
Max'm	1.50	0.73	0.87	0.60			
Min'm	0.69	0.25	0.27	0.06			
Diff.	0.81	0.48	0.60	0.54			

The wide variations found in the above table are without doubt due to differences in manipulation, as the samples were very carefully prepared, and were as nearly uniform as it is possible to make them. The temperature of the oven and the manner of cooling before weighing have a great influence on the moisture result. There are water ovens which do not furnish a temperature of 100° C. even with the water boiling and the control of an air bath is always more or less imperfect. If the moisture determinations are made either on watch glasses, using one watch glass as a cover while cooling, or in shallow aluminum, or glass weighing dishes provided with a tightly fitting stopper, so that the sample can be stoppered while cooling and weighing, and if the temperature of the oven is fully 100° we believe that the results would agree much more closely.

PHOSPHORIC ACID.

Official Gravimetric Method.—This method is too well known to require an outline. It is described in Wiley's "Principles and Practice of Agricultural Analysis," Vol. 2, page 16. The figures in this and the following tables refer to the percentage of P_2O_5 on the wet basis.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.32	27.27	31.50	26.43
2	31.41	27.32	31.06	26.60
3	31.67	27.35	31.37	26.73
4	31.49	27.44	31.33	26.77
5[2]	31.83	27.82	31.32	27.08
6	31.88	27.74	31.40	26.90
7	31.96	27.52	31.46	26.72
8	31.47	27.23	31.34	26.48
9	32.01	28.03	31.80	26.81
10	31.50	28.13	32.13	27.20
11	32.20	27.51	31.33	26.89
12[3]	31.08	26.95	30.94	26.52
13[4]	30.91	26.72	30.59[1]	26.01
14	31.18	27.24	31.00	26.46
15	31.61	27.10	31.00	26.20
16	31.84	27.05	31.92	27.31
17	31.79	27.10	31.77	27.24
18[5]	31.72	27.47	31.18	26.71
19	31.29	27.05	31.31	26.53
Average	31.59	27.37	31.40	26.71
Maximum	32.20	28.13	32.13	27.31
Minimum	30.91	26.72	30.94	26.01
Difference	1.29	1.41	1.19	1.30

[1] Omitted from average.

[2] We quote an interesting paragraph from the methods of Wiley and Hoffman, "We believe that many rock solutions contain silica in a fine condition which passes through the single paper used by most analysts and believe it advisable to filter all rock solutions through at least three papers of the S & S No. 597 grade before measuring off the aliquot. With some samples we have used six papers in order to obtain a clear solution."

[3] Yellow ppt. formed in the cold and digested for 30 minutes at 60–65° C.

[4] Yellow ppt. is washed six times with 2 per cent. HNO_3 (50 cc. each time). Magnesium ammon. phosphate is burned for one hour in muffle furnace and for fifteen minutes in blast-lamp.

[5] Sulphuric acid with about 4 g. mercuric oxide is used as the solvent.

To some extent the variations here may be due to departure from the official method but probably most largely to differences in details not included in the description of this method. Six different factors for converting magnesium pyrophosphate to P_2O_5 were reported. The factors were as follows: 0.6375, 0.63757, 0.6376, 0.638, 0.63965, 0.6397, the theoretically correct factor being 0.63757, although 0.6376 is close enough.

Volumetric Method, sometimes called Pemberton's Method.—The solution of the yellow precipitate in standard potassium hydrate and titration by a standard acid solution is its chief feature. An outline of this method may be found in Bureau of Chemistry, Bulletin No. 107, page 4.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.58	27.53	31.29	26.53
2	31.65	27.47	31.19	26.50
3	32.20	28.25	31.85	27.75
4	32.10	27.90	31.86	27.26
5	31.40	27.40	31.55	26.50
6	31.88	28.33	31.78	27.36
7	31.50	27.10	31.30	26.45
8	31.00	26.90	30.88	26.18
9	31.99	27.20	31.83	27.43
10	31.39	27.30	31.00	26.39
Average	31.67	27.54	31.45	26.83
Maximum	32.20	28.33	31.86	27.75
Minimum	31.00	26.90	30.88	26.18
Difference	1.20	1.43	0.98	1.57

Citrate Method.—Based upon the power of alkaline ammonium citrate to hold in solution the salts of iron aluminum, and calcium, thus permitting the direct precipitation of phosphoric acid as ammonium magnesium phosphate. Described fully in Wiley's "Principles and Practice of Agricultural Analysis," Vol. 2, page 57.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.35	27.01	31.36	26.57
2	32.42[1]	27.44	32.03	26.98
3	31.33	27.59	32.07	26.91
4	33.34[1]	28.41[1]	31.86	26.82
5	33.50[1]	29.30[1]	31.70	27.00
Average	31.34	27.35	31.80	26.86
Maximum	31.35	27.59	32.07	27.00
Minimum	31.33	27.01	31.36	26.57
Difference	0.02	0.58	0.71	0.43

Gladding Method.—In this method the ammonium phosphomolybdate is dried and weighed, the percentage of P_2O_5 being calculated from this weight.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.53	27.25	31.35	26.43
2	31.54	27.43	31.08	26.31
Average	31.54	27.34	31.22	26.37
Difference	0.01	0.18	0.27	0.12

IRON AND ALUMINUM OXIDES.

Smith or Modified Von Grueber Method.—The rock is dissolved in hydrochloric acid and the iron is determined by titrating a portion of this solution with potassium permanganate. A second portion of the original solution is added to an excess of strong KOH solution, which while precipitating the iron retains the aluminum in solution as potassium aluminate. From this solution the aluminum is separated as phosphate by the addition of HCl and ammonia.

[1] Omitted from average.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.56	3.27	2.66	4.54
2	7.12	3.39	2.48	4.17
3	7.56	3.60	2.49	4.59
4	7.43	3.52	2.56	4.67
5	7.09	3.07	2.67	3.91
6[2]	7.76	8.43[1]	2.81	5.21[1]
7	7.65	3.62	2.55	4.60
8	7.31	3.27	2.47	4.23
9	7.54	3.16	2.47	4.80
10	7.53	3.49	2.81	4.40
11	6.94	3.22	2.28	3.93
12	5.60[1]	4.12	2.56	3.95
Average	7.41	3.43	2.57	4.34
Maximum	7.76	4.12	2.81	4.80
Minimum	6.94	3.07	2.28	3.91
Difference	0.82	1.05	0.53	0.89

Gladding Method.—In this method the separation of the alumina by means of a KOH solution is somewhat similar to that of the Smith method. The precipitation of the aluminum phosphate, however, is made by a neutral solution of ammonium acetate as in the acetate method. The iron is determined by titration with a standard solution of potassium bichromate.[3]

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.35	2.42	2.42	4.10
2	7.17	3.06	2.46	4.36
3	7.36	4.84[1]	2.41	2.61[1]
4	7.63	4.37	2.36	4.54
Average	7.38	3.28	2.41	4.33
Maximum	7.63	4.37	2.46	4.54
Minimum	7.17	2.42	2.36	4.10
Difference	0.46	1.95	0.10	0.44

Acetate Method.—The HCl solution of the rock is nearly neutralized with ammonia, after which are added a few centimeters of ammonium acetate and heated to 70° C., which completely precipitates the iron and aluminum phosphates. This is dissolved in HCl and reprecipitated in the same manner. One-half of the combined weight of phosphates is usually taken to represent the Al_2O_3 and Fe_2O_3.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.49	3.58	2.51	4.30
2	7.02	2.73	2.19	4.10
3	8.76	3.92	3.31	5.20
4	7.85	8.56	2.85	4.49
5	6.95	2.90	2.19	4.08
Average	7.33	3.28	2.43	4.24
Maximum	7.85	3.92	2.85	4.49
Minimum	6.95	2.73	2.19	4.08
Difference	0.90	1.19	0.66	0.41

Glaser Method.—In this method the lime is first removed by converting into calcium sulphate by means of sulphuric acid in the presence of strong alcohol. After filtering, a portion of the solution is evaporated to expel alcohol, diluted and heated to boiling. Ammonia, added until alkaline precipitates the iron and aluminum as phosphates.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	6.72	3.60	2.59	4.07
2	6.20	3.06	2.13	3.20
3[1]	8.32	6.16[1]	2.71	4.26
4	7.33	3.75	2.40	4.27
5[4]	6.20	6.50[1]	2.30	3.00[1]
Average	6.97	3.47	2.43	3.95
Maximum	8.32	3.75	2.71	4.26
Minimum	6.20	3.06	2.13	3.20
Difference	2.12	0.69	0.58	1.06

Jones Variation of Glaser Method.—This is practically the same as the Glaser method, except that about ½ the quantity of sulphuric acid and 1½ times the amount of alcohol are used.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1[2]	7.37	8.37[1]	2.63	4.43
2[2]	7.82	8.00[1]	2.12	4.64
Average	7.59		2.37	4.53
Difference	0.45		0.51	0.21

Wyatt's Method.—The phosphates of iron and aluminum are precipitated from a portion of the original solution by making slightly alkaline with ammonia and then acid with acetic acid. The ppt. is filtered, dissolved, and reprecipitated in the same way.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1[3]	7.27	2.20	2.27	4.10
2	6.22	3.30	2.54	2.94
3[2]	6.20	7.42[1]	2.43	5.00
Average	6.56	2.75	2.41	4.01
Maximum	7.27	3.30	2.54	5.00
Minimum	6.20	2.20	2.27	2.94
Difference	1.07	1.10	0.27	2.06

COMPARISON OF AVERAGES.

Method.	No. 1.	No. 2.	No. 3.	No. 4.
Smith	7.41	3.43	2.57	4.34
Gladding	7.38	3.28	2.41	4.33
Acetate	7.33	3.28	2.43	4.24
Glaser	6.97	3.47	2.43	3.95
Jones Mod. of Glaser	7.59	....	2.37	4.53
Wyatt	6.56	2.75	2.41	4.01

EFFECT OF DIFFERENT SOLVENTS IN THE DETERMINATION OF IRON AND ALUMINA.

We have received from Messrs. L. P. Brown and Company, Nashville, Tenn., an interesting comparison showing the effect of different solvents in the determination of iron and alumina, which we give in the following table:

Sample.	Solvent	Fe_2O_3.	Al_2O_3.	Fe_2O_3 and Al_2O_3
No. 1	100 cc. HCl (1:1)	3.40	4.16	7.56
Tenn. Brown	50 cc. HCl conc.	3.51	3.51	7.02
10 g.	30 cc. HCl conc. and 20 cc. HNO_3 conc.	3.74	3.73	7.47
No. 2	100 cc HCl (1:1)	1.31	2.29	3.60
Tenn. Blue	50 cc. HCl conc.	1.52	1.49	3.01
10 g.	30 cc. HCl conc and 20 cc. HNO_3 conc.	6.38	1.47	7.85
No. 3	100 cc HCl (1:1)	1.10	1.39	2.49
Fla. Pebble	50 cc. HCl conc.	1.26	1.40	2.66
10 g.	30 cc. HCl conc. and 20 cc HNO_3 conc.	1.58	1.47	3.05
No. 4	100 cc. HCl (1:1)	3.11	1.48	4.59
So. Car.	50 cc. HCl conc.	3.20	1.39	4.59
10 g.	30 cc. HCl conc. and 20 cc. HNO_3 conc.	3.52	1.43	4.95

Note especially the effect of aqua regia on No. 2 sample and that in all cases the addition of HNO_3 seems to increase the Fe_2O_3. This is due to the presence of pyritic iron which remains undecomposed when hydrochloric acid is used. The effect of aqua regia as a solvent can also be seen in several of the tables under iron and alumina, especially in the case of No. 2, or Tennessee blue rock.

[1] Omitted from average.

[2] Five g. rock are treated in a platinum crucible with 4 cc. H_2SO_4 and 20 cc. HF. This is evaporated to dryness on a steam bath and fused with Na_2CO_3. Fusion dissolved in dil. hydrochloric acid and water.

[3] Ref. *J. Am. Chem. Soc.*, **18**, 721.

[4] Solvent: Aqua regia.

[1] Omitted from average.

[2] Solvent: Aqua regia.

[3] Aqua regia used as solvent for Nos. 1, 3 and 4. HCl (1:1) used on No. 2.

This is one of the most important questions to be decided and for the present we recommend the use of hydrochloric acid (1:1) as a solvent in the determination of iron and alumina.

In some experiments conducted by Dr. F. B. Carpenter, of the Virginia-Carolina Chemical Company, it was found that the length of time in which the solution is boiled makes a material difference in the results of iron and alumina and for that reason they have adopted a definite amount of acid (1:1) to 2 g. of rock, boiled for one hour on the hot plate.

CONCLUSION.

It should be remembered that our main object is to agree upon uniform methods to be used in settlement analyses. Regarding the reports received as expressions of opinions by the chemists named, it becomes evident in the case of phosphoric acid, which method should be selected. The results of the volumetric and the Gladding methods are excellent, but at this time there are not sufficient reasons for substituting either of these for the present official method.

In the case of the methods for iron and alumina, the results indicate that the methods most generally used are those employing a KOH solution in the separation of the iron from the alumina, *viz.*, the Smith and the Gladding methods. In the other methods, the iron and alumina was determined by weighing the combined phosphates. Of these the acetic and the Glaser methods are the most important, and it is our opinion that some modification of the acetate method could be worked out which would be extremely satisfactory, as it appeals to chemists on account of its simplicity as compared with other methods. The close agreement of the reports on iron and alumina is noticeable, excepting a few results and those in which aqua regia was employed.

We recommend that for referee work the Official Gravimetric Method be used for phosphoric acid, and that in the methods now in use for iron and alumina, the solvent be hydrochloric acid (1:1) until the question of the effect of pyritic iron in acidulating can be definitely solved. The methods for iron and alumina will be investigated further with a view to the adoption of one of the methods as standard for our work.

We believe that a strict adherence to uniform details in these methods will yield very much better results and that it is essential for our fertilizer chemists to agree upon these details. We are, therefore, preparing a set of methods to include moisture, the official gravimetric method for phosphoric acid, and the various methods for iron and alumina, which will give complete details as far as possible. These methods will be submitted to all the chemists who previously worked on the samples, with the request that the work be gone over again, following in detail the instructions given. With these additional results at hand, we shall be able to submit a definite proposal concerning the adoption of Association methods.

In the preparation of these methods we shall welcome the suggestions of those interested in this subject.

C. F. HAGEDORN,
C. H. DEMPWOLF, JR.,
F. B. CARPENTER.

A TEST FOR SKIN PULP IN TOMATO CATSUP.

During an investigation of several different brands of tomato catsup for artificial color, a peculiar result was noticed on the addition of lead subacetate. Some catsups became absolutely solid while others formed only a slight flocculent precipitate. It was thought at first that some adulterant was the cause of the large precipitate, but a thorough investigation failed to detect any. Accordingly, tests were made on tomatoes, both green and ripe, fresh from the garden. It was found that whole tomato pulp, after cooking, normally yields a dense white precipitate with lead subacetate while the skins, carefully freed of pulp and boiled with water, yield no precipitate with the same reagent. Tests were then made on commercial pulps of known composition. In every case, whole pulp yielded a dense precipitate. In some samples, supposed to be skin pulps, a certain amount of precipitate was formed, probably due to careless peeling of the original tomatoes, not enough, however, to convey the impression that whole pulp exclusively had been used. The method adopted was as follows: A small quantity of the sample was diluted with three times its volume of water and filtered. The filtrate was treated with a few drops of lead subacetate solution, sp. gr. 1.25. Whole pulp yielded a dense white precipitate, while skin pulp gave only a slight flocculent precipitate. Knowing well the variations possible in the original tomatoes, it is not claimed that any quantitative estimation of the proportion of whole and skin pulp used can be obtained from the volume of the precipitate. However, it is believed that the test furnishes a reliable guide as to the quality of any catsup. The absence of any precipitate is proof of the use of skin pulp.

H. W. COWLES, JR.

THE COMMITTEE ON ANALYSIS OF FATS, SOAPS AND GLYCERINE.

A few weeks before the New Haven meeting of the American Chemical Society (June 30 to July 2, 1908) a subcommittee was appointed by Dr. W. F. Hillebrand, chairman of the Committee on Uniformity in Technical Analysis, for the purpose of developing standard methods for the analysis of fats, soaps and glycerine. The committee thus appointed consists of: W. D. Richardson, chairman; J. W. Loveland, secretary; R. E. Devine, D. Wesson, A. C. Langmuir, B. T. B. Hyde, W. H. Low, and Ernest Twitchell. The first meeting of the committee was held at the Graduates Club, New Haven, Conn. June 30, 1908. It was decided that the scope of the committee for the present be limited to the consideration of the analysis of such materials as are commonly bought and sold. It was further decided that the immediate attention of the committee should be directed toward the analysis of the following products for the constituents named, definitions to be decided upon when necessary: Fats and oils, moisture and volatile matter, free fatty acids, titer, unsaponifiable matter, metallic soaps, gross impurities; Cotton Seed Foots, total fatty acids and resinous matter, moisture; Cotton Seed Black Grease, free fatty acids, moisture, resinous matter, unsaponifiable matter; Cotton Seed Foots Soap, total fatty acids, moisture, combined alkali, free alkali, matter insoluble in alcohol, sodium chloride, unsaponifiable matter; Crude Glycerine, glycerol, organic impurities; Dynamite Glycerine, specific gravity, organic residue, sodium chloride, ash, fatty acids, silver nitrate test; Chemically Pure Glycerine, con-

sideration of methods postponed for the present. The following special committees were appointed to consider the various subdivisions of the main subject: Fats and Oils, Mr. Loveland, chairman, and Mr. Richardson; Cotton Seed Foots and Cotton Seed Black Grease, Mr. Wesson, chairman, and Mr. Twitchell; Cotton Seed Foots Soap, Mr. Low, chairman, and Mr. Wesson; Crude and Dynamite Glycerine, Mr. Langmuir, chairman, Mr. Devine and Mr. Hyde. The general plan of procedure includes the consideration of the best methods at present in use for the various determinations and co-operative work on standard samples by analysts skilled in the various lines of work using the methods selected; the formulating of definitions of words requiring definition; and the drawing up of standard methods of analysis.

All analysts who are interested in the work or who are willing to co-operate in it are invited to correspond with the chairmen of the special committees, or with the chairman of the subcommittee. W. D. RICHARDSON.

QUOTATIONS.

CHILEAN NITRATE FIELDS.

(From *Daily Consular and Trade Report*, No. 3327, Nov. 10, 1908.)

The following report concerning the nitrate fields of Chile, and the manner of producing nitrate of soda and iodine, is furnished by Consul Rea Hanna, of Iquique:

The Camarrones Valley, in latitude 19° south, marks the northern limit of any appreciable deposits of nitrate, and Carizal Valley, in latitude 26° south, marks the southern limit. Within this zone, which has a length of some 500 miles, deposits of salitre, or nitrate of soda, have been discovered in five different districts as follows, running from north to south: (1) The pampa of Tarapacá, included between south latitudes 18° 30′ and 21°, with the ports of Iquique, Caleta Buena, Junin, and Pisagua, and a railway running from Iquique, to Pisagua, connecting all the important nitrate plants; (2) the pampa of Toco, on the banks of the small river Loa, which furnishes power for some of the plants, in latitude 22° south, with the port of Tocopilla, and a railway to the principal nitrate works; (3) the pampa of Antofagasta, in latitude 23° south, traversed by the railway from Antofagasta, the port, to Oruro, Bolivia; (4) the pampa of Aguas Blancas, in latitude 24° south, with the port of Caleta Coloso; (5) the Taltal Pampa, between south latitudes 25° and 26°, with the port of Taltal.

Crystallized nitrates appear in very small quantities only, being found in commercially valuable amounts in a mixture of chlorides, sulphates, and other salts, together with earth and rock, commonly called caliche.

In technical works on this subject, the local names of the strata are usually employed. The accompanying sketch gives an idea of the average formation in the Pampa of Tarapacá, which is the most important of the nitrate fields.

STRATA IN WHICH NITRATE IS FORMED.

The "chuca" is a loose layer of from 8 to 16 inches in thickness, and is composed, generally speaking, of decomposed volcanic rock.

The "costra" is a mixture of feldspar and other similar rocks or the clay and sand products of their disintegration, together with sulphates of calcium, sodium, and potassium, and chloride of sodium, and is from 3 to 10 feet in thickness. It is never less than 1 foot thick and never more than 18 or 20 feet. It is composed of the same materials as the chuca, with the addition of salts which act as cement, making it very hard in places. The composition is principally of clay, salt, nitrate of soda, and sulphates of magnesium, calcium, and sodium.

The caliche, with the exception of very rich lays, is, like the costra, a mixture of detritus united by a cement of salts. The insoluble constituents of caliche are fragments of volcanic rock and quartz gravel, from the size of fine sand to pieces as large as a human head. Caliche is a general term applied to all classes of materials containing nitrate, and varies greatly from a chemical standpoint; it is the customary term for the material taken from the strata rich in nitrate.

GROUPS AND COMPOSITION.

On account of its formation and origin it may be classed under four headings:

(1) In the form of deposits in strata, in veins, and in pockets resting on loose material and quaternary detritus, and covered with a layer of conglomerate salts, gravel, and loose earth, these strata measuring from 8 inches to 26 feet in thickness.

(2) In the form of impregnations which the nitrate and its accompanying salts have left in the decomposed surfaces of volcanic rock.

(3) In the form of fillings in chalky deposits.

(4) In the form of efflorescence on the surface of salt fields.

Of these four groups the first one is the only form having importance in the production of nitrate.

There is a great variation in the composition of caliche as well as in the appearance, and the nitrate of soda contained runs from 15 per cent. to 65 per cent. of the total weight, the average running from 25 per cent. to 35 per cent. Chloride of sodium is always present and at times is found in banks as pure crystalline salt.

IODINE, CONGELO, AND COBA.

Iodine is the important by-product and occurs as iodate of calcium, called "laurita," and a double salt composed of iodate of calcium and chromate of sodium, called "dietzeita." These are the most important forms; the iodides do not appear. The existence of chromic acid gives the caliche an orange color and indicates a high lay of iodine. The proportion of iodine runs from 0.06 per cent. to about 5 per cent., 2 per cent. being considered a favorable amount.

The "congelo" is found in varying quantities in all districts, and consists of a substance containing compact crystalline masses of chloride of sodium, of iodine, or of sulphates.

The "coba" is, as a rule, loose earth slightly moist, mixed with small rocks or pebbles. Salitre and other salts are contained in very small quantities. The coba rests on volcanic rock, and in places has a thickness of 300 feet.

The nitrate district is situated in the rainless belt, and although heavy fogs are often present it seldom rains.

EXTRACTION OF NITRATE OF SODA.

Before beginning actual work in the calicheras, or areas of deposit of the caliche, an exploration is made by means of drilling to find the limits of the area of ground rich in

nitrates. If it is impossible to determine the lay by inspection, a blast is placed to further open up the workings. An approximate assay is then made, an expert being able to assay 50 to 70 samples per day.

The process of working the calicheras and the extraction of the nitrate of soda has varied little since the beginning of the industry. A trench is opened by means of continued blasting, and the caliche is sorted out of the mass by men trained to the work. The caliche is then loaded on mule carts and carried to the extraction plant, locally called the "máquina." Some of the oficinas have small trains and locomotives running from the calichera to the máquina to perform this part of the work. On an average one man can sort out from 4,000 to 4,500 pounds of caliche per day. On arriving at the plant the caliche is dumped into a receptacle leading to the crushers, from which it is carried in cars up a cable incline to the cachuchas, or boiling tanks.

Here the process consists of a lixiviation of the crushed caliche, at a determined temperature, in a separation or settling of the insoluble parts from the solution obtained, and, finally, in a precipitation of the nitrate of soda from the oversaturated solution by means of crystallization. In spite of the fact that this process appears mechanically simple, the practical application presents many difficulties.

SOLUBILITY AND BOILING.

The solubility of the nitrate of soda varies greatly, on account of the different combinations of other salts present in the caliche. While at ordinary temperatures 85 parts of nitrate dissolve in 100 parts of water, the solubility in the presence of chloride of sodium lowers to 53 parts, dissolving at the same time 26 parts of the chloride. At a temperature of 120° C., 100 parts of water dissolve 220 parts of nitrate, while the amount of chloride is reduced to 15 parts. Sulphate of sodium and the other salts exert a similar influence, although not as great.

The usual type of cachucha or boiling tank is made of sheet iron and is from 28 to 32 feet in length, from 6 to 9 feet in width, and of equal depth. Some 6 or 8 coils of perforated steam pipe serve to heat the caliche and to furnish water for the solution, as well as keeping the mixture agitated. About 8 inches from the bottom is a perforated iron plate acting as a sieve to keep the refuse, called ripio, from leaving the tank with the solution.

This boiling process continues, at a temperature predetermined by assays of the caliche, for a period of from twenty to twenty-four hours, when the solution is discharged into a settling tank, where it remains for a short time, usually fifteen minutes to half an hour, from which it is led through pipes or troughs to the crystallizing tanks.

These are usually about 15 feet square with a slanting floor, being 33 inches deep on one side and 27 inches on the other, with outlet cocks for the agua vieja, or mother liquid, at the lowest point. After the solution has been allowed to stand some five or more days, the water is drawn off to be used again in the boiling tanks, thus avoiding the loss of the percentage of nitrate still in solution.

SHIPPING METHODS—ANALYSES.

When the sun and atmosphere have completely dried the nitrate it is sacked, loaded on flat cars, and shipped to the nearest port. Analyses of the ordinary nitrate as produced by this process show the following variations:

Component parts.	Per cent.	Per cent.
Nitrate of soda	94.164	94.245
Nitrate of potassium	1.763	1.249
Chloride of sodium	.933	1.180
Iodate of sodium	.010	.017
Perchlorate of potassium	.282	.239
Sulphate of magnesium	.219	.303
Chloride of magnesium	0.289	0.342
Sulphate of calcium	.102	.041
Insolubles	.138	.174
Moisture	2.100	2.210
Total	100.000	100.000

Commercial usage calls everything salitre, except moisture and insolubles.

The assaying of the samples of caliche is by a process which gives an error of 2 or 3 per cent. which serves its purpose, and besides being sufficiently accurate is very rapid.

COST OF INSTALLATION.

In an estimate made some time since it was stated that, in general, to produce from 50,000 to 100,000 Spanish quintals (1 quintal = 101.61 pounds) per month the plant investment will be about £1 per quintal, or about $4.80 per 100 pounds.

An estimate on this basis of the cost of an installation to produce 100,000 quintals per month is as follows:

Buildings, including houses for 550 laborers, of whom 250 are married, $45,440; extraction plant, complete machinery, $266,700; mules, harness, carts, merchandise for store, sacks, coal, etc., $133,150; total, $445,290.

On account of the increased price of materials and the rise in freights from 30 to 50 per cent. must be added to this estimate for the present time.

The cost of nitrate of soda alongside vessels in the ports runs from $1.58 to $1.82 per Spanish quintal, depending on the richness of the deposits and the amount of other salts in the caliche.

The method of the extraction of salitre has been severely criticised, both as to process and administration, on account of the great waste caused by the amount of workable area covered by the refuse materials after the blasts and on account of the incomplete extraction of the nitrate from the caliche worked. Many managers are making a serious study to determine better methods of operation.

PAPER CURRENCY, OIL FOR FUEL, AND AVAILABLE NITRATE DEPOSITS.

The fluctuation in the value of the Chilean currency appears to be a source of great disturbance, having fallen from 25 cents to 14 cents and lately risen again to 22 cents within the past year. The laborers, being paid in local currency, become dissatisfied when, on account of varying exchange, the prices rise while the wages remain the same. Several strikes have resulted, notably the one in December, 1907, when some 15,000 men left the Tarapaca Pampa and came down to Iquique to make their demands on the agents of the oficinas.

The introduction of oil, instead of coal, as a fuel is making great changes. A company at Caleta Buna has successfully used Peruvian oil for some time, and recently an American oil company has erected a 7,000-ton storage tank in both Tocopilla and Taltal. In these ports it is used in many oficinas, as well as on the railways. Oil will probably be introduced into Iquique in a short time, as the managers

of the oficinas using it in Tocopilla and Taltal claim a saving of from 20 per cent. to 30 per cent. over the use of coal.

The last report of the delegacion fiscal, or board of government engineers, estimates the quantity of nitrate still available to be worked as follows, in Spanish quintals: Tarapaca Pampa, 740,000,000; Antofagasta, Toco, and Taltal pampas, 4,103,000,000. Total, 4,843,000,000.

MARKETING THE OUTPUT.

The Antofagasta Pampa was expected to develop rich deposits, and heavy investments were made in the matter of extraction plants, but exploitation discovered that instead of lying in regular strata, as in Tarapaca, the caliche is deposited in irregular patches and in pockets which make successful operation of the oficinas a very difficult matter.

The total output of the iodine has been handled for some time by a London firm acting for the nitrate combination, and a movement is now on foot to centralize the sale of nitrate in the same manner, eliminating brokers and middlemen. The success of this scheme depends on the continuance of the present nitrate combination, which terminates, according to the agreement at its formation, on March 31, 1909.

On account of the drop in the price of nitrate, the combination decided that this year's quota of permitted production should be reduced to 47 per cent. of the original amount, so that only 39,500,000 Spanish quintals will be produced during the year ending April 1, 1909. Of this amount, 85 per cent. may be exported between April 1 and December 31, 1908.

CATALYTIC REDUCTION OF FATS AND OILS.

(From *Science*, **28**, 572, October 23, 1908.)

About four years ago it was shown by Paal and Amberger[1] that palladium could be obtained in a particularly active colloidal aqueous solution (hydrosol). Subsequently the senior author demonstrated[2] that this liquid, in presence of hydrogen, was capable of causing the catalytic reduction of nitrobenzene. The work has now been extended to include certain other substances,[3] the most generally interesting of which are oleic acid and a number of oils.[4]

The acid, in the form of its potassium salt, is dissolved in water and mixed with a small quantity of the palladium solution, the liquid being then introduced into a gas burette containing hydrogen, standing over mercury. Absorption of the gas commences immediately and the reaction is completed in a few hours. No heating is required. Oleic acid, under these conditions, is converted almost quantitatively into stearic acid. Castor oil, dissolved in a mixture of ether and alcohol, is transformed into a crystalline fat, which softens at 69° and melts at 77°.

The behavior of olive oil is very peculiar. It combines with three times the quantity of hydrogen which was anticipated from its behavior with iodine. The product, which in general properties resembles that from castor oil is still capable of combining with iodine. Unless, therefore, some flaw can be shown to exist in the experiments, it will be necessary to revise our ideas of the processes which take place during the ordinary testing of oils and fats with iodine (Hübl's method).

[1] *Ber.*, **37**, 124 (1904); **38**, 1398 (1905).

[2] *Ibid.*, **38**, 1406, 2414 (1905); **40**, 2209 (1907).

[3] *Ibid.*, **41**, 2273.

[4] *Ibid.*, **41**, 2282 (1908).

Train oil absorbed about 30 per cent. more hydrogen than was anticipated. The yield of solid fat was quantitative. Before reduction the train and olive oils were converted into emulsions with water and a little gum arabic.

These results promise to be of great importance to plant physiologists, because the reactions proceed under conditions comparable, in a number of respects, with those under which similar or identical products are formed in nature. To the industrial chemists, the results may also prove to be of considerable value; a reasonably cheap method of transforming liquid oils into solid fats has been much sought after. J. BISHOP TINGLE.

MCMASTER UNIVERSITY,
TORONTO, CANADA.

INDIAN INDIGENOUS DYES.

(From *Daily Consular and Trade Reports*, No 3318, Oct. 30, 1908.)

Consul-General William H. Michael, of Calcutta, submits the following results in tests of natural dyestuffs of India in comparison with chemical dyes:

Mr. E. R. Watson, connected with the Asiatic Society of Bengal, has been experimenting with dyes, both indigenous and synthetical, and appears to demonstrate the superiority of the former over the latter so fully and clearly that it would seem the contention in favor of the latter would cease. Mr. Watson experimented with ten vegetable dyes, *viz.*, turmeric, or huldi (Curcuma longa); safflower, or kusum (Carthamus tinctorius); spanwood, or bakam (Caesalpinia sappair); palas (Butea frondosa); annatto, Orleans, or lakkam (Bixa orellana); majisto (Rubia cordifolia); kamala (Mallotus philippinensis); singher, or harsinghar (Nyctanthes arbor-tristis); jackwood, jack, or kanthal (Artocarpas integrifolia), and lac dye.

He followed the native methods of dyeing, and had no occasion to resort to any European as opposed to India method. He used silk cloth purchased from the Rajshahi diamond jubilee industrial schools, and his success was greater than in the case of experiments in dyeing cotton fabrics. The conclusions he arrives at are that the indigenous dyes of Bengal are considerably more useful for dyeing on silk than for cotton dyeings, and that the dyeings obtained are frequently considerably faster on silk than on cotton. This, taken in conjunction with the fact that many of the commonly used synthetic dyes do not give fast dyeings on silk, causes the indigenous dyes to compare much more favorably with their synthetic adversaries in this field than was the case of the field of cotton dyeing. He says:

The shades obtained from bakam on a tannin-iron mordant, from manijisto, from lac, kamala, and jackwood may be said to have all-round good fastness, as in no respect does any one of these dyeings come lower than III in the scale. Thus of 10 dyestuffs examined 5 have yielded dyeings which may be characterized as all-round good. Of the 12 synthetic dyestuffs used for comparison only 4, *viz.*, alizarine, primuline, chrysophenine, and magdala red are capable of yielding dyeings which may by the same criterion be similarly characterized.

My work would lead me to form a somewhat higher opinion of the value of the kamala as a silk dye than has been recorded by A. G. Perkin. The dyeings with lac proved to be faster to soaping even than the synthetic dyes which were fastest

in this respect. In fact, the general fastness of lac dyeings made it appear to me a matter of surprise that this material has been so completely superseded by synthetic dyes, the more so as it is necessarily obtained as a by-product in the purification of lac, a material for which there is an ever rapidly increasing demand.

CONCRETE RAILWAY TIES.

(From *Daily Consular and Trade Reports*, No. 3326, Nov. 9, 1908.)

In the preparation of the following report concerning the manufacture of reenforced cement railway ties in Italy Consul Chapman Coleman, of Rome, says that the information was furnished by the Italian state railway authorities, the Gabellini Cement Company, and others:

The Italian Government has ordered 300,000 of these ties, which are now in course of construction. A few thousand of such ties, ordered for experimental purposes, were constructed by the Gabellini company some years ago, and have been used on the railroad from Castellamare-Adriatico to Ancona. As a result of the trials to which the ties were subjected a new design, to be employed in executing the present large order, will replace the old. The principal change will, it is understood, be found in the introduction into the concrete mass of a larger number of the reenforcing metallic bars, of reduced diameter, in the new design of ties.

The cost of a concrete tie is estimated a[illegible] $1.20, and it is believed that its endurance will be t[illegible] to four times as great as that of a wood tie. A tie will weigh about 286 pounds, inclusive, of the weight of the metallic reenforcement, about 28 pounds. A comparison of the respective cost and value of concrete and wooden ties would no doubt give different results in the United States from those afforded in the Italian estimates, owing to varying conditions in the two countries affecting local cost of materials and manufacture, endurance, etc. The belief is largely entertained here that the concrete tie will eventually entirely replace wood tie.

SPECIFICATIONS FOR REENFORCED CONCRETE TIES.

The following are the principal features of the technical specifications respecting the furnishing of ties of reenforced cement to the Italian state railways:

The materials to be used in construction are normal Portland cement, sand in grains of two sizes, round iron bars, and braces of wood. The cement must not contain impurities of any sort, nor more than 2 per cent of sulphur in any state of oxidation. The tests of the purity of the cement must not show variations in volume nor excessive heat during the process of setting. Tests mechanically conducted with normal sand, which has been kept for twenty-eight days under water, must show a coefficient of resistance to strain of not less than 10 kilos per square meter and a coefficient of resistance to compression of not less than 100 kilos to the square centimeter. The sand must be calcareous-silicious, containing about 30 per cent. of silex, must be nonbituminous, and must consist of grains of two sizes the half of the quantity necessary must be passed through a screen with circular holes of 5 millimeters in diameter; the other half must be normal sand.

At equal prices preference will be given to artificial sand obtained by the crushing of calcareous-silicious stone, providing the products respond to the above indicated conditions and the stone resists breaking under a pressure of not less than 500 kilos to the square centimeter. The round reenforcing bars of the ties must support three bending tests at a temperature of 20 degrees of cold. The use of zinc iron is excluded. Braces must be of wood of strong fiber (male oak, bitter oak, hornbeam, walnut, acacia, etc). The wood must be well seasoned and derived from trees felled while green and at the proper season of the year. They must be thoroughly permeated with tar oil and must not contain cracks or other defects which may prejudice the use for which they are intended. No tolerance will be given in the dimensions of the braces; they will be provided at the cost of the furnishing firm and will be subjected to examination by the agents of the state railways before acceptance.

In the construction of the ties a paste or admixture will be employed which shall contain a cubic meter of sand (one-half large, the other normal), 750 kilos of normal Portland cement, with the addition of a little water to give the mass a moist consistency. The sand will be washed with clean water, and so carefully and thoroughly that when fresh water is again applied it will be found to remain perfectly clear.

This mass must be diligently compressed around the armature, either by hand or mechanically. For compression by hand work, pestles of a weight not inferior to 750 grams will be employed, and the material to be compressed will be applied in strata of not less than 2 centimeters in thickness and will be continued until complete adjustment is attained. For mechanical compression a pressure not inferior to 25 kilos per square centimeter must be employed and applied at the same time to the entire tie.

The ties, as soon as formed and without having been subjected to any bending strain, must be placed upon an even, unbroken surface and covered with powder tufa or earth material, and must be kept constantly moist for at least fifteen days. After twenty days the ties may be sacked, but must be protected from the action of atmospheric agents for a further period of at least ten days. The ties may be entirely submerged in water, but only after setting has taken place

The agents of the administration of state railways will supervise the manufacture of the ties and will assure themselves that the conditions of these specifications are observed, and will therefore have the right of free entrance to the plant of the furnishing firm at all times. They will also be entitled to break open one tie for every thousand in order to ascertain whether the reenforcement has been done with iron bars of the prescribed diameter; and whenever it is found that bars of a less diameter have been used, the entire quantity under manufacture will be rejected.

The furnishing firm is required to guarantee the ties for one year from the date of the last receipt of consignment and to replace or refund the price of any ties which it has become necessary to remove during the period of guaranty because of their unserviceable nature, resulting from defective manufacture; and action in this regard is to be left to the exclusive judgment of the administration of the state railways.

Diagrams showing the detailed Italian construction and manufacture and test of concrete railway ties may be seen at the Bureau of Manufactures.

[1] *J. Soc. Chem. Ind.*, **14**, 460 (1895).

BOOK REVIEWS.

Metallurgy: A Condensed Treatise for the Use of College Students and Any Desiring a General Knowledge of the Subject. By HENRY WYSOR, B.S. Assistant Professor of Analytical Chemistry and Metallurgy in Lafayette College. 8vo. 308 pages, illustrated. The Chemical Publishing Co., Easton, Pa. Price, $3.00

In the preface the author states that the book is offered as a guide to the Science of Metallurgy. "The general scheme is the setting forth of the principles involved in the subject; the description of process or groups of processes and such reasoning as is calculated to show the applications of natural law in the operations considered. The ideal is the embodiment of the history, practice and philosophy of Metallurgy in a single volume admitting only such matter as is essential to the student."

The book is divided up into chapters as follows: I. Physical Properties of the Metals, 9 pages. II. Refractory Materials and Fluxes, 6 pages. III. Theory of Combustion and Thermal Measurements, 8 pages. IV. Classification and Description of the Fuels—the Natural Fuels, 7 pages. V. The Prepared Fuels, 15 pages. VI. Ore Dressing, 14 pages. VII. Furnaces, 5 pages. VIII. Iron-Ore and Properties, 12 pages. IX.–XVI. Iron Smelting, Cast Iron, Wrought Iron, Steel, Crucible, Bessemer and Open-Hearth, Further Treatment, 93 pages. XVII.–XIX. Copper, etc. Reverberatory, Blast Furnace and Pyritic Smelting. Wet Methods. Copper Refining, 39 pages. XX.–XXII. Lead, Ores, etc. Reverberatory, Hearth and Blast Furnace, Smelting, Lead Refining and Desilverization, 22 pages. XXIII. Zinc, 9 pages. XXIV. Tin and Mercury, 5 pages. XXV. Silver, 13 pages. XXVI. Gold, 14 pages. XXVII. Nickel, Aluminium, Manganese and Rarer Metals, 10 pages. XXVIII. Alloys, Manufacture, etc., Welding and Plating, 13 pages. There are 88 illustrations.

To bring the whole field of metallurgy within this small compass requires great condensation and a careful elimination of all but the essentials. This has been done by Mr. Wysor in very clear and simple language, producing a well balanced book, such as is necessary for the beginner. On the whole, the details given are accurate but occasionally we find matter that is very much out of date. For example, in the table of Physical Constants of Common Metals on page 9, the melting points are mostly those of Roberts-Austen's "Introduction to Metallurgy." This could have been improved by introducing the later and more accurate determinations of Burgess and others. The few lines devoted to hardening carbon on p. 17 are quite misleading. On the same page we are told that silicon combines with iron probably in several proportions, whereas it would have been as easy and better to have stated that Guertler and Tammann have shown the existence of only two compounds, namely Fe_2Si and FeSi.

The chapters devoted to the metallurgy of iron and steel are the best in the book. Under copper the section on roasting is not so good, the choice of mechanical furnaces not bearing the proper relationship to their relative importance; the difference between uses of the reverberatory smelter (or the blast furnace) to produce black copper or blister versus matte for Bessemerizing is not emphasized as it ought to be. Under lead it is hardly right to class the alloying of lead with copper along with that of lead with gold or with silver and iron can not be said to alloy with lead. The roasting of lead ores is poor, no mention being made of the newer methods of pot-roasting now so important. Under electrolytic refining the Betts' process ought to have been given as the example for it is now in operation at Trail B. C., Grasselli, Ind., and elsewhere.

In the sections on gold the chlorination process is treated mainly from the standpoint of treatment in vats and the barrel process, which for years was the main method onCripple Creek Ores, is neglected. In the cyanide process the space devoted to the Pelatan-Clevici process could have been used to better advantage in giving a short account of the present prevalent methods of fine grinding and vacuum filters, etc.

The section on alloys is the one to be most criticized. The ideas are old and we are told (p. 283) that Matthiessen's view, that metals pass into an allotropic form when they alloy, is the generally accepted one. Considering the great advance in our knowledge of alloys due to the application of the methods of physical chemistry and the work of the students of Tammann, Bancroft and others, this part of the book is considerably out of date.

Taken as a whole, the book gives us what the author intended a clear and concise account of the elements of metallurgy. WILLIAM CAMPBELL.

Electro-Metallurgy. By JOHN B. C. KERSHAW. D. Van Nostrand Company, New York. 1908. pp. xv + 303. Illustrations. Price, $2.00 *net*.

A popular treatise on the production of metals and other articles of commercial value by use of the electric current. This book is one of the Westminster series of books on practical subjects designed to meet the needs of the non-technical reader. The object is well attained and the result is a very readable and instructive volume. As in most works by English authors, a comprehensive history of the development of each industry is included. The various processes used in the different industries are fully considered, the faults in the earlier methods, with the remedies and improvements receiving marked attention. Costs of production are given throughout and these are so fully itemized that possibilities of cost reduction are at once apparent. It is to be regretted that in this edition, intended largely for use in the United States, values should be expressed in pounds and pence and weights generally in long tons.

Attention is called to the fact that the lack of available water power in the United Kingdom and in Germany is responsible for the comparatively slow development of electrometallurgical industries in these countries, and the hope is expressed that with the utilization of the waste gases of blast furnaces for production of electric current, the iron centers of these countries may also become centers of electrometallurgical industry. On pages 116 and 117 it is stated that "the anode copper used in these two refineries (Anaconda and Great Falls) is practically the same in composition, since it is obtained by smelting the ores of the famous mines of the Butte district of California." As a matter of fact, the Butte mines, as is well known, are in Montana, and while at Great Falls, anodes are cast direct from the converters, at Anaconda they receive a preliminary refining before being cast into anodes. On page 51, Deutsche is spelled without an "s," but on the whole typographical or other errors are remarkably few, and the book is well made up.

It is unfortunate that only a name index is provided, for in

these days when one frequently needs to refer to some matter in a hurry, a table of contents can hardly take the place of a good index. Taken altogether, Electro-Metallurgy is just such a book as one would wish to recommend to his non-technical friends for interesting and instructive information on a subject of great importance. F. W. TRAPHAGEN.

Der Betriebs-Chemiker, Ein Hilfsbuch für die Praxis des Chemischen Fabrikbetriebes. DR. RICHARD DIERBACH, Fabrikdirektor. Second Edition. Julius Springer, Berlin. 1908. pp. xii + 340. Price, 8 marks.

This work, the first edition of which was published in 1903, has reached a second edition in 1908, and has been enlarged, rearranged and in part rewritten in the present edition. It is designed primarily to meet the needs of the industrial chemist, the works manager, the chemical manufacturer and the chemical engineer. Following a general introduction which treats of the problems of the industrial chemist, his relation to the operating force and his duties as scientific leader, the work takes up the various aids in industrial technique, considering first, materials of construction; next, mechanical aids; third, power machinery, including heat, water, and electric motors, transmission devices and various types of conveyors and conveyances. The second general division of the work considers plant construction in brief and according to general principles, without entering too much into detail. The third part discusses the special work of the industrial chemist, considering first the work within the laboratory, second the development of industrial processes, and third the construction and installation of apparatus in the chemical industry. The fourth division is devoted to protective devices against accidents and risks, and the fifth division considers methods of work. The sixth, seventh and eighth divisions consider respectively, by-products, calculations and the storage and shipment of products. The work is well arranged and well printed and bound. It is needless to say that it satisfies a want and should be in the possession of all industrial chemists. W. D. RICHARDSON.

The Chemical Analysis of Iron. By ANDREW ALEXANDER BLAIR. Seventh edition pp. 343. J. B. Lippincott Co. Price, $4.00.

The main changes from the sixth edition, 1906, occur in the methods for gas analysis (p. 310) and the revision of the table of factors and atomic weights in general from the values for 1908 as given by the International Committee.

An account of the Volumetric Method for Nickel (p. 193), Sargent,[1] and of the method for the separation of vanadium, molybdenum, chromium and nickel in steel (p. 209) have been added.

Binding and printing are of the same excellent quality, though the book is now a trifle thicker, due to the thicker paper used. WILLIAM CAMPBELL.

Laboratory Guide of Industrial Chemistry. By ALLEN ROGERS. D. Van Nostrand Co., New York. Price, $1.50 net.

This book is designed to serve as a text-book to students who are attempting to acquire a knowledge of industrial processes in a short space of time in a technical school. The book is divided into ten chapters covering general processes, inorganic preparations, dyeing, commercial organic compounds, pigments and alkalies, paints and varnishes, soap, leather manufacture, wood fibre and paper, and data for calculations. The illustrations used are of modern apparatus and are valuable for explanatory purposes. Much of the material in the chapter on inorganic preparations is the same as that found in text-books on inorganic chemical preparations. The matter of expecting the student to estimate cost is new and is desirable. We wish, however, that the student had been requested to keep fuller data on such items as fuel required for evaporation, time spent in carrying on the operations, and include these items in the cost, instead of adding 20 per cent. to cost of materials, freight and containers. The descriptions of processes are good. In the chapter on dyeing, following general instructions, several typical examples are given in detail. The chapter on chemical organic compounds is of value in showing some of the relations of pure organic chemistry to industrial chemistry. We notice that in the chapter on soap, no mention is made of the fact that glycerin is a product of saponification, and can be recovered from the spent lye. In the chapter on wood fibre and paper, the paper-making process is given in a way such that it may be carried out in the laboratory. The best chapter in the book is the one on the dyeing of textile fibres and we regret that the author did not keep up the standard set in this chapter in the remainder of the book. On the whole, the book is well written and the subjects are well presented. It will be of much service in the hands of the instructor in industrial chemistry who is trying to correlate this laboratory work with a series of lectures. H. McCORMACK.

Soils and Fertilizers. By HARRY SNYDER, B. S., Professor of Agricultural Chemistry and Soils, University of Minnesota. Third edition. The Macmillan Co., New York. 1908. pp. 350. Price, $1.25 net.

The third edition of Professor Snyder's successful work on "Soils and Fertilizers" will be appreciated by those who have had occasion to use the earlier editions. The demand for a third edition is sufficient index to the usefulness of the work. The present edition has been revised and enlarged and as the author states in the preface, includes "all the topics and laboratory experiments relating to soils as outlined by the Committee on Methods of Teaching Agriculture, of the Association of Agricultural Colleges and Experiment Stations." While the work is the outgrowth of Professor Snyder's own teaching experience and is designed principally as a text-book, it can be read with profit and interest by the farmer and the general scientific reader. It is well arranged, compact, clear and suitably printed and bound. It should be in the library of all interested in the subject.

W. D. RICHARDSON

The Manufacture of Lubricants, Shoe Polishes and Leather Dressings. By RICHARD BRUNNER, translated from the sixth edition by Chas. Salter. Scott, Greenwood & Co., London. D. Van Nostrand Co., New York. 1906. Cloth, small 8vo. pp. 176. Price, $3.00 net.

This little book reminds the reviewer of a similar smaller one by the same publishers for which they had the courage to charge three dollars and a half. How a firm which publishes such valuable works as those by Hurst, Andes, Hausbrand, McIntosh, and others, can follow such practices and issue books of this kind is hard to understand.

The work would seem to have been written at about the time of the discovery of petroleum, or even earlier, and never

[1] *J. Am. Chem. Soc.*, **21**, 854.

properly revised since. Some of the statements are wrong, for example on page 30, the statement is made that the American mineral oils are made from the distillation of lignite tar.

A whole chapter is devoted to caoutchouc greases—which are not favorably regarded at the present time: another to oiling devices, nearly half of which is occupied with the description of two ordinary oil cans, to the omission of modern means as oil pumps, oiling rings and pins. The author states that neatsfoot oil is obtained from pig's feet and that there are but two oils suitable for clock oils, olive and bone oil, having never heard of black fish and other fish oils used for the purpose.

Among the curious and worthless formulae are those for lubricating greases containing ground glass, infusorial earth and ground brimstone; clock oils made from heavy tar oils, sewing machine oils containing rubber, and a fish oil leather grease (p. 157) containing 30 per cent. of carbolic acid to "preserve it from going rancid."

Few, if any, of the formulae are modern and most of them could probably be duplicated by a novice in the business, and the book would be dear at one-third the price.

A. H. Gill.

Liquid and Gaseous Fuels and the Part They Play in Modern Power Production. By Vivian B. Lewis, F.I.C., F.C.S. D. Van Nostrand Company, New York. 1907. pp. xiv + 334. Price, $2.00.

It can scarcely be said that the title of the book thoroughly expresses or covers the contents. It is true that both liquid and gaseous fuels are discussed, and the method and apparatus for the determination of calorific power of all kinds of fuel described. In ten ample chapters are treated: the Principles of Combustion from a Chemical Standpoint; The Source and General Composition of Fuels, Solid, Liquid and Gaseous; Methods and Apparatus for Determination of Calorific Power and Description of the Units Involved; Petroleum, its History, Sources and Properties; Lamps and Burners for Production of Light and Heat with Liquid Fuel; the History of Coal Gas, its Constituents and Calorific Value; Water Gas, its History, Value, Production and Application. The book closes with a chapter on comparison of the thermal value of fuels, the efficiency of the internal combustion engine, the treatment and utilization of peat as fuel, solar heat, its fixation and utilization. and "fuel of the future."

It would seem that the first and last chapters might be usefully curtailed. The principles of combustion have been exhaustively elsewhere in works readily available, reducing thus the value of the first chapter, while in discussing the "fuel of the future" in the last chapter, the suggestion that a half consumed substance like alcohol may eventually take the place of other fuels now in use when, or as long as, the vegetable materials available for production of alcohol are at hand and may be produced at the rate of from one to several tons per acre, seems almost ridiculous. The reputed Kansas practice of burning the whole ear of corn, grain and cob, seems better, while the utilization of corn stalks, the straws, the growth of those crops yielding large produce as syrup, ramie, etc., all of which have for equal weight a higher thermal value than alcohol, would be still more advantageous. As long as the sun shines and broad acres may be cultivated, crude vegetable materials will be at hand and the "fuel of the future" is much more likely to be found in such raw materials as come directly from the field, than in the half-consumed products of fermentation.

Wm. McMurtrie.

The Power Handbooks. Hill Publishing Co. $1.00 each, post-paid.

(1) Knocks and Kinks. Cause, detection and cure for many of the commonest of these troubles of the engine man. Compiled and written by Hubert E. Collins. pp. 137.

(2) Erecting Work. Compiled and written by Hubert E. Collins. pp. 140.

(3) Pipes and Piping. Compiled and written by Hubert E. Collins. pp. 140.

These little books are not in any sense comprehensive treatises of the subjects of which they treat. On the other hand, they contain various special and more or less disconnected chapters connected with the engineering subject specified in the title, and some of these chapters are reproduced from Power and are written by various experts and some are written especially for the series by the compiler and author. We note such chapters as Hauling Heavy Machinery; Moving a Cylinder; Building up a Fly-Wheel; Vibration in Steam Pipes; A Color Scheme for Pipe Lines; Effect of Superheated Steam on Cast Iron Valves and Fittings; Causes of Knocks; Some Curious Knocks; How a Noisy Piston Valve was Cured; etc. These titles will suggest in a general way the purpose and scope of the volumes, and that they will be found useful to the power plant man up to the limit of their scope, is certain.

W. D. Richardson.

Methods and Devices for Bacterial Treatment of Sewage. By William Mayo Venable, M.S., M.I.S.C.E., etc. First edition. pp. 231. John Wiley & Sons, New York: 1908. Price, $3.00. The successive chapters of the book are as follows: I. Introduction. II. Sources of Information about Sewage Apparatus. III. Aërobic Treatment of Crude Sewage. IV. Mechanical Removal of Sludge. V. Anaërobic Treatment of Sewage. VI. Intermittent Contact Systems. VII. Automatic Discharging Devices. VIII. Percolating Filters. IX. Summary of Engineering Principles Regarding the Design of Sewage Purification Works. X. Difficulties Experienced in Some Actual Installations. XI. Suggested Designs to Meet Typical Conditions.

Chaps. III. to VIII. inclusive discuss sewage purification in its various aspects. The several methods of treatment considered in historical order are kept distinct in the presentation. Extensive use has been made of drawings of U. S. patents both old and recent. The best feature of the book is the historical treatment of the various devices, especially patented ones which have been used for sewage disposal. The descriptions of the various automatic discharging devices in Chap. VII. is especially complete. In the chapter on Percolating Filters it does not seem as if enough attention has been given to the description of the various sprinkler nozzles in common use for distributing the sewage. Neither does the reviewer find any description of the aphidian distributor in common use in England. As has been stated above, the book contains very little about the chemistry and bacteriology of sewage and of the biological processes which take place during the process of purification. In Chaps. IX., however, are given several paragraphs which embody some of the conclusions of such studies by other workers. The

writer gives the results of his experience in connection with the sewage disposal plants at Des Moines, Ia., and Fort Leavenworth, Kansas, and in the last chapter of the book works out a design consisting of septic tank, deep filter bed and shallow contact bed for a typical case. The book is well illustrated, especially with cuts of siphons. It contains a reprint of an interesting plate by Leonard Metcalf, C. E., entitled the "Antecedents of the Septic Tank."

ROBERT SPURR WESTON.

NEW BOOKS.

The Mineral Industry. Vol. XVI for 1907. 1127 pages, illustrated. Cloth. Price, $10.00. NewYork: Hill Publishing Co.

Coal: Its Occurrence, Value, and Methods of Boring. By R. REDMAYNE. 215 pages, illustrated. Cloth. Price, $2.00 net. New York: Longmans, Green & Co.

Public Water Supplies. By E. EUGENE TURNEAURE and RUSSELL HARRY LUMAN. (Requirements, resources and the construction of works; with a chapter on pumping-machinery.) By. D. W. Meat. 825 pages, illustrated. Cloth. Price, $5.00. New York: John Wiley & Sons.

Color Photography and Other Recent Developments of the Art of the Camera. By C. HOLME. 123 pages, over 100 illustrations. Paper. Price, $3 net. New York: John Lane Co.

The Geology of Coal-Mining. By WALCOT GIBSON. (Arnold's geological series; general ed. J. E. Marr.) 351 pages, illustrated. Cloth. Price, $2.50. New York: Longmans, Green & Co.

Das Laboratorium fur angewandte Chemie der Universitat Leipzig in seiner neuen Gestaltung. By E. BECKMAN. M. 2.50. Leipzig: Guelle & Meyer.

Manuel practique de Galvanoplastic et de depots electrochemiques (Encyclopedie industrielle). By A. BROCHET. Paris: J. B. Bailliers & Fils. Frs. 5.

Water Softening and Purification of Hard and Dirty Waters. By HAROLD COLLETT. 2nd edition, revised. 177 pages, illustrated. Cloth. Price, $2.00. New York: Spon & Chamberlain

Wax Craft. All about Beeswax, its History, Production, Adulteration and Commercial Value. By T. W. COWAN. Illustrated. Low. Cr. 8vo. 172 pages. 2 S net.

Gold and Silver. By WALTER R. CRANE. Comprising an economic history of mining in the United States, the geological and geographical occurrence of the precious metals, with their mineralogical associations, history and descriptions of mining and extraction of values, and a detailed discussion of the production of gold and silver in the world and the United States. 727 pages; illustrated. Cloth. Price, $5.00 net. New York: John Wiley & Sons.

Die Chemie and Industrie der Kalisalze (Aus "Deutschlands Kalibergbau," Festschrift zum X. Allgem. deutschen Bergmannstage zu Eisenach, 1907). By E. ERDMANN. Herausgeg, von der Konigl, Preuss. Geologischen Landesanstalt, Berlin.

Der gegenwartige Stand der chemischen und elektro-chemischen Industrie auf dem europaischen Kontinent. By P. P. FEDOTJEFF. 229 Seiten, mit 62 Fig. Sonderabdruck aus den "Ber. d. Polyt. Inst. St. Petersburg."

Process Cost Accounts. By H. GARRY and C. A. STANLEY. London: Gee and Company.

Iron, its Sources, Properties and Manufacture. By W. H. GREENWOOD. With numerous engravings and diagrams. 255 pages, illustrated. Cloth, $1.00. Philadelphia: David McKay.

Thermodynamics of Technical Gas Reactions. By DR. F. HABER. Translated by Arthur B. Bamb, Ph.D. London, New York, Bombay and Calcutta: Longmans Green & Co.

Steel, its Metallurgy and Mechanical Treatment. By F. W. HARBORD and J. W. HALL. Third edition, revised. 758 pages, with illustrations. Price, $9.00 net. Philadelphia: Lippincott.

Papierprufung. Eine Anleitung Pzum Untersuchen vonapier. By WM. HERSBERG. Dritte vermehrte und verbesserte Auflage. Berlin: Julius Springer.

Handbuch d. Spiritusfabrikation. By M. MAERCKER. 9 vollstand. neubaarb. Aufl., Herausgeg. von Prof. Dr. M. Delbruck mit 284 Textabb. w 2 Tafeln. Berlin: P. Parey. M. 28.

Dairy Laboratory Guide. By CHAS. MELICK, B.L.A., M.Sc. 129 pages with 52 illustrations. Price, $1.25. New York: D. Van Nostrand Co.

Industrie des Metaux secondaires et des terres rares (Encyclopedie scientifique publiee sous la direction du Dr. Toulouse.) By P. NICOLARDOT. Frs. 8, Paris: O. Doin.

The Value of Sodium to Plants by reason of its Protective Action; (also) On the Effects of Certain Poisonous Gases on Plants. By W. J. V. OSTERHOUT. Berkeley, Cal. University of Cal. 331–340 pages. Q. pap. 10 cents.

Traite Complet d'Analyse Chimique Appliquée Aux Essais Industriels. By J. Post and B. Neumann. Deuxième edition allemande et augmentee de nombreuses additiona par le Dr. L. Gautier. Tome second, premier fascicule. 199 pages. Frs. 6. Paris: Librairie Scientifique A. Hermann.

Leather Industries, Laboratory Book of Analytical and Experimental Methods. By. H. RICHARDSON PROCTOR. Second edition, revised and enlarged. 475 pages with illustrations. Cloth. Price, $7.50. New York: Spon and Chamberlain.

Die Untersuchung und Verbesserung des Wassers fur alle Zwecke seiner Verwendung. By W. ROTTMANN. Geh. M. 2.20; geb. M. 2.60. Hanover: Dr. Max Janecke.

Soils and Fertilizers. By HARRY SNYDER. Third edition. 350 pages with illustrations. Cloth. Price, $1.25 net. New York: Macmillan Co.

The Paper Mill Chemist. By H. P. STEVENS. 280 pages with illustrations. Cloth. Price, $2.50 net. New York: D. Van Nostrand Co.

The Metallurgy of Iron. By T. TURNER. One of a series of treatises on metallurgy written by associates of the Royal School of Mines, edited by Sir W. Roberts-Austen, with numerous illustrations. Third edition, revised and enlarged. 463 pages. Cloth. Price, $1.25. Philadelphia: Lippincott.

Handbuch der Chemie und Technologie der Ole und Fette. Herausgegeben von Dr. L. Ubbelohde. Verlag von S. Hirzel in Leipzig. I. Band, geh. M. 39; geb. M. 33.

Recipes for the Preserving of Meats, Fruit and Vegetables. By E. Wagner. Translated by C. Salter. 119 pages. Cloth. Price, $2.50. New York: D. Van Nostrand Co.

Beet Sugar Manufacture and Refining. Vol. II., Evaporation, Graining and Control. By L. S. Ware. 647 pages, 225 illustrations. Cloth. Price, $5.00. New York: John Wiley & Sons.

A Preliminary Report on the Manganese Deposits of Georgia. By Leonard T. Watson. (Atlanta, Ga. S. W. McCallie.) 195 pages, with illustrations, maps and drawings. (Georgia Geological Survey Bulletin.) Paper. Price, 12 cents.

The Art of Paper Making. By Alexander Watt. Third edition, 260 pages with illustrations. Cloth. Price, $3.00. New York: D. Van Nostrand Co.

On the Plantation, Cultivation and Curing of Para Rubber. By H. A. Wickham. 96 pages. Ill. K. Paul. 3s. 6d.

Cyanide Processes. By Eugene B. Wilson. Fourth edition, revised and enlarged. 249 pages with illustrations. Cloth. Price, $1.50. New York: John Wiley & Sons.

Bestimmung von Teerfarbstoffen in Farblackfabrikation verwendeten. By Georg Zerr, zwei Teile in einem Band gebunden, Dresden. Teerfarbstoffe in ihrem Verhalten gegen bestimmte Reagenzien. Steinkopff & Springer.

Cement Laboratory Manual. By L. A. Waterbury. A manual of instructions for the use of students in cement laboratory practice. Illustrated. 12mo. Cloth. 129 pp. New York: D. Van Nostrand Co. 1908. Price, $1.00.

Modern Power Gas Producer Practice and Applications. By H. Allen. A practical treatise dealing with the gasification of various classes of fuels by the pressure and suction systems of producer. 136 illustrations. 12mo. Cloth. 334 pp. London. 1908. Price, $2.00 net.

Bacteria in Relation to Country Life. By J. G. Lipman. 506 pages, illustrated. Cloth. New York: D. Van Nostrand Co. Price, $1.50 net.

Annual Reports on Progress of Chemistry for 1907. Vol. IV. Issued by the Chemical Society. 8vo. Cloth. Price, $2.00 net. Volumes I., II. and III. previously published. Each, $2.00 net. New York: D. Van Nostrand Co.

The Brewers' Analyst. By R. D. Bailey. A systematic handbook of analysis relating to brewing and malting, with interpretations of analyses, polariscopical, microscopical and biological works. Cloth. 423 pages, 133 illustrations. New York: D. Van Nostrand Co. Price, $5.00 net.

Fire Assaying. By E. W. Buskett. A practical treatise on the Fire Assaying of Gold, Silver, and Lead, including description of appliances used. Cloth. Illustrated. New York: D. Van Nostrand Co. Price, $1.25 net.

Practical Paper-making. By G. Clapperton. A manual for paper makers and owners and managers of paper mills, to which is appended useful tables, calculations, data, etc., with illustrations reproduced from micro-photographs. Cloth. Illustrated. Second edition, revised and enlarged. New York: D. Van Nostrand Co. Price, $2.50 net.

Sewage Disposal Works. By H. P. Raikes. Design, construction and maintenance. Cloth. 402 pages, 72 illustrations. New York: D. Van Nostrand Co. Price, $4.50 net.

Technical Thermodynamics. By Dr. A. Zeuner. Translated from the fifth completely revised German edition of Dr. Zeuner's original treatise on Thermodynamics. By Prof. J. F. Klein, Lehigh University. Cloth, illustrated. (To be published in two volumes, for sale together.) Vol. I., 460 pp. Vol. II., 556 pp. New York: D. Van Nostrand Co. Price, $8.00 net.

Illinois State Geological Survey, Bulletin No. 8 Year Book for 1907. Compiled by H. Foster Bain. Director State Geological Commission. 391 pp. 23 illustrations. Cloth binding. Springfield, Ill.: Phillips Bros. 1908.

Per Cent Tables for Oil in Cottonseed Products. By Chas. H. Herty. 50 pp. Cloth binding. Chapel Hill, N. C.: The University Press.

SCIENTIFIC SOCIETIES.

WINTER MEETING, AMERICAN CHEMICAL SOCIETY.

The Winter meeting of the Society will be held in Baltimore, Md., December 27th to January 1st, inclusive. The meeting will be in affiliation with the American Association for the Advancement of Science and the Biological Section will hold a joint session with the Society of Biological Chemists.

The following members have consented to preside over Sections and to aid in the preparation of the program for the meeting:

Agricultural and Food Chemistry	H. J. Wheeler.
Biological Chemistry	J. J. Abel.
Inorganic Chemistry	C. H. Herty.
Organic Chemistry	S. F. Acree.
Pharmaceutical Chemistry	Edw. Kremers.
Chemical Education	H. P. Talbot.
Fertilizer Chemistry	F. B. Carpenter.
Physical Chemistry	G. N. Lewis.
The Division of Industrial Chemists and Chemical Engineers will also hold a meeting presided over by the Chairman of the Division	A. D. Little.

Members desiring to present papers are requested to send title and brief abstracts to one of these persons or to the Secretary of the Society with the exception of the Section of Chemical Education, where a special program is being arranged. Titles of all papers received before November 20th will appear on the preliminary program, which will be sent to all members.

The current year has been one of the most successful in the history of the Society, as shown by many important improvements in its organization and by the large increase in membership. The Society has grown more this last year than any two previous years in its history and now approximates four thousand members.

The publications of the Society have been issued without exception on time, and they have acquired a standing which has insured the success and continuation of Chemical Abstracts. The new Journal of Industrial and Engineering

Chemistry will be sent to all members next year and the first number will be issued early in December.

The two years of President Bogert's administration have brought many important improvements in the organization and the industrial chemists owe chiefly to his enthusiasm and energy, ably seconded by the Council, the fact that they now have the Division of Industrial Chemists and Chemical Engineers firmly established and have a journal with an unusually able board of editors.

The idea of organizing the Society into Divisions, fostered by President Bogert since his first inauguration, seems to have taken a fast hold upon the membership, and committees are considering the advisability of organizing Divisions of Food Chemists, Fertilizer Chemists, Pharmaceutical Chemists, Organic Chemists, and Physical Chemists. Some of these plans may come to maturity at the Winter meeting.

The Chicago meeting and the New Haven meeting were eminently successful and were largely attended.

Local Sections have been established during the year at Schenectady, N. Y., and Louisville, Ky. Two other Local Sections are now in process of formation.

During the year a number of important committees have been appointed and reports made, all of which are published in the Proceedings. The Committee on Chemical Education, the Committee on Institute of Chemistry and the Committee on Conservation of our Natural Resources are now considering matters of the utmost importance to the Society and the profession.

CHAS. L. PARSONS,
Secretary.

14th GENERAL MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY.

NEW YORK CITY, OCTOBER 30, 31, 1908.

PROGRAM.

Thursday, October 29th.

At the Chemists' Club.

8 : 30 P.M.—Meeting of the Board of Directors, in the Library, second floor.

Friday, October 30th.

In Doremus Lecture Theatre, College City of New York.

9: 00 A.M.—Prof. Baskerville, Director of the Laboratory, will introduce President J. H. Finley, who will welcome the Society.

Reading and Discussion of Papers.

(1) The Use of a Mercury Cathode in the Determination of Metals. A. Harold Porter and Francis C. Frary.
(2) The Passivity of Nickel and Iron. E. P. Schoch.
(3) Equilibrium in Standard Cells. G. A. Hulett.
(4) Chemical Energy. J. E. Mills.
(5) The Formation of Nitric Acid from Air by Means of Low-Voltage Direct Current. G. W. Morden.

12 : 30 P.M.—Luncheon, by invitation of the Staff of the Department of Chemistry of the College of the City of New York, in Alumni Hall, Main Building (Ladies invited).

1 : 40 P.M.—A twenty-minute organ recital, complimentary to the Society, by Prof. Samuel A. Baldwin, Head of the Department of Music, in the Great Hall, second floor, Main Building.

In Doremus Lecture Theatre

2 : 00 P.M.—Reading and Discussion of Papers.

(6) Electrolytic Corrosion of the Bottom of Oil Tanks. A. A. Knudson.
(7) The Corrosion of Underground Structures. Albert F. Gang.
(8) The Function of Oxygen in the Corrosion of Metals. W. H. Walker.
(9) The Theory of Electrolytic Paints. W. D. Bancroft.
(10) Simple Methods for the Prevention of Electrolytic Corrosion. Maximilian Toch.

7 : 30 P.M.—Informal Subscription Dinner, at Reisenweber's, Columbus Circle, 58th Street and 8th Avenue, New York City. Ladies especially invited to attend. Subscription $3.00.

Saturday, October 31st.

At Chemists' Club, 108 W. 55th Street.

9 : 00 A.M.—Reading and Discussion of Papers.

(11) The Lash Steel Process and the Electric Furnace. F. A. J. Fitzgerald.
(12) Utilization of Power Stations for Electrochemical and Electrothermal Processes during Periods of Low Load. E. A. Sperry.
(13) Electrochemical Loads and the Central Station. John Meyer.
(14) Correct Methods of Measuring Stray Currents. Clayton H. Sharp.
(15) The Latent Heat of Vaporization of Zinc. W. McA. Johnson.

1 : 00 P.M.—Luncheon at Hotel Cumberland, 54th Street and Broadway (Price, 75 cents). Ladies invited.

2 : 00 P.M.—Leave Hotel Cumberland for excursions and visits. Ladies invited to participate.

Leave West 23rd Street at 2 : 25 P.M. for Balbach Smelting and Refining Works, Newark, N. J., where the processes of smelting and refining of copper, lead, silver and gold may be seen.

8 : 30 P.M.—A "Smoker" tendered to the American Electrochemical Society by special invitation of the Chemists' Club, in the Assembly Room of the Club, 108 West Fifty-fifth Street.

The meeting of the American Electrochemical Society, the program of which appears above, was especially well attended. About two hundred members and guests were registered. At the first session Dr. Hulett's paper on Equilibria in Standard Cells, proved of great interest, being a continuation of his work on the standard cell, giving detailed results and a number of his measurements to outline causes of variation in voltage and methods for obtaining constant results. Mr. Morden's paper detailed a number of experiments made at the University of Toronto, on the formation of nitric acid from air by means of low voltage, direct current. The afternoon meeting was devoted to a symposium on the "Corrosion of Iron," and was productive of a lively discussion. Mr. Fitzgerald's paper was on the "Production of Steel by the Lash Process in the Héroult Furnace," Mr. Fitzgerald showed the economies of this process, which consist in the smelting of briquettes made of ore, cast iron, coke and lime, the economy consisting in the relatively large amount of ore that can be used in this process over that used in the open-hearth furnace. Mr.

Fitzgerald showed that with this process, as operated in the Héroult furnace, one ton of steel can be produced at 0.27 h. p. years per ton of steel.

Mr. W. McA. Johnson's paper was devoted to a mathematical calculation of the latent heat of vaporization of zinc, which he gives at 388 large calories. This figure has not been determined experimentally, but using the same method of calculation for mercury, he finds 61.8 large calories, as against 62 determined experimentally.

In the afternoon a very interesting excursion was made to the works of the Balbach Smelting and Refining Company.

The next meeting of the Society is to be held in May, 1909, at Niagara Falls. W. R. WHITNEY.

THE WESTERN ASSOCIATION OF TECHNICAL CHEMISTS AND METALLURGISTS.

The Board of Control has under consideration the determination of the place for holding the next annual meeting of the Association. Two places have been proposed, one to accept the invitation of the University of Colorado Section and hold the meeting at Boulder, Colorado, the other to make Denver the general meeting place with visits of a day each to Boulder and to Golden, where the program would be furnished largely by the members of the Association connected with the University and the School of Mines respectively.

Former annual meetings have been held at Denver, Salt Lake City, and Deadwood, South Dakota.

Blanks are in circulation calling for nominations for the office of President, the present incumbent, Mr. W. G. Swart, having served the constitutional term. Three members of the Board of Control are also to be nominated, to succeed J. C. Bailar, Golden, Colo., W. B. Bishop, Grand Forks, B. C., and C. A. Rose, Denver, Colo.

COLORADO SECTION.

Following its custom, the Colorado Section, after its summer vacation, gave for its first fall meeting the annual dinner. The dinner this year was an "Old-Fashioned Beefsteak Dinner" and about seventy-five guests were present. After the dinner, which was given at the Metropole Hotel, Professor Robert Kennedy Duncan, of the chair of Industrial Chemistry in the University of Kansas, gave a very interesting talk on Temporary Industrial Fellowships, and Professor Lucien J. Blake, Consulting Engineer of the Submarine Telegraph Company, of Boston, delivered a scholarly address on the Theory of Electrolysis.

F. W. TRAPHAGEN.

PROGRAM OF THE TWENTY-FIFTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By direction of the Executive Committee of the Association, the Twenty-fifth Annual Convention will be held at Washington, D. C., November 12 to 16, inclusive, 1908. The meeting will be called to order at 9 o'clock, A.M. at the Annex Hall of the Normandie, on McPherson Square, Fifteenth and I Streets.

The following resolution was adopted at the 1907 meeting:

That one day of the convention be devoted entirely to the reading of papers and their discussion, and that for this purpose the convention be divided into three sections covering the same subjects as the present committees on recommendations, and that all papers to be read in these sectional meetings be referred to the proper committee with full power to reject the same or assign places to them in the program sent to all members prior to the meeting.

In the program submitted provision is accordingly made that the final day of the meeting be devoted to the reading of papers.

ORDER OF BUSINESS.

THURSDAY.

Morning Session.

Food Adulteration. H. E. Barnard, Indianapolis, Ind.

Colors. H. M. Loomis, Seattle, Wash.

Saccharine Products. Arthur Given, Washington, D. C.

Fruit Products. C. B. Cochran, West Chester, Penn.

Wine. Julius Hortvet, St. Paul, Minn.

Beer. H. E. Barnard, Indianapolis, Ind.

Distilled Liquors. L. M. Tolman, Washington, D. C.

Vinegar. Chas. H. Hickey, Boston, Mass.

Flavoring Extracts. E. M. Chace, Washington, D. C.

Spices. A. L. Winton, Chicago, Ill.

Baking Powder and Baking Powder Chemicals. E. L. Redfern, Lincoln, Nebr.

Appointment of Committee C on recommendations.

Afternoon Session.

Food Adulteration—Continued.

Meat and Fish. F. C. Weber, Washington, D. C.

Fats and Oils. H. E. Bishop, Indianapolis, Ind.

Dairy Products. Herman Lythgoe, Boston, Mass.

Cereal Products. E. F. Ladd, Fargo, N. Dak.

Vegetables. W. L. Dubois, Buffalo, N. Y.

Condiments other than Spices. E. M. Bailey, New Haven, Conn.

Cocoa and Cocoa Products / Teas and Coffee } A. G. Woodman, Boston, Mass.

Preservatives. W. D. Bigelow, Washington, D. C.

Determination of Water in Foods. E. W. Brown, Washington, D. C.

Separation of Nitrogenous Bodies. L. L. Van Slyke, Geneva, N. Y. (Milk and cheese proteids.)

Meat Proteids. P. F. Trowbridge, Columbia, Mo.

Vegetable Proteids. E. B. Hart, Madison, Wis.

FRIDAY.

Morning Session.

Appointments of committes on resolutions, on nominations, on amendments to the constitution, and Committees B and C on recommendations of referees.

Medicinal Plants and Drugs. L. F. Kebler, Washington, D. C.

Tannin. F. P. Veitch, Washington, D. C.

Insecticides. C. C. McDonnell, Washington, D. C.

Inorganic Plant Constituents. H. D. Haskins, Amherst, Mass.

President's address. Harry Snyder, St. Anthony Park, Minn.

Afternoon Session.

Soils. S. D. Averitt, Lexington, Ky.

Phosphoric Acid. J. M. McCandless, Atlanta, Ga.

Potash. B. B. Ross, Auburn, Ala.

Report of Committee C on Recommendations of Referees.

Report of Committee on Food Standards. Wm. Frear.

Report of Committee on Testing Chemical Reagents. L. F. Kebler.

SATURDAY.

Morning Session.

Dairy Products. J. M. Bartlett, Bartlett, Me.

Foods and Feeding Stuffs. J. P. Street, New Haven, Conn.

Sugar—general analytical methods. A. H. Bryan, Washington, D. C.

Molasses Methods. H. P. Agee, Audubon Park, La.

Chemical Methods. Fritz Zerban, Audubon Park, La.

Report of Committee A on Recommendations of Referees.

Afternoon Session.

Report of Committee B on Recommendations of Referees.

Report of Committee on Revision of Methods. J. K. Haywood, Washington, D. C.

Report of Committee on Fertilizer Legislation. H. W. Wiley, Washington, D. C.

Report of Committee to present the question of unification of terms to the International Congress of Applied Chemistry. R. J. Davidson, Blacksburg, Va.

MONDAY.

Miscellaneous Papers and their Discussion.

Section A (phosphoric acid, potash, nitrogen, soils, ash, and insecticides).

The Rate of Decomposition of Organic Matter in the Soil. J. G. Lipman, New Brunswick, N. J.

A Discussion of Methods for' Determining the Availability of Phosphoric Acid in Thomas Phosphate Powder (basic slag phosphate). G. D. Leavens, New York City.

Section B (dairy products, foods and feeding stuffs, sugar, tannin, and medicinal plants and drugs).

Babcock Standard. E. B. Holland, Amherst, Mass.

The Unification of Polarimetric Observations. C. A. Browne, New York City.

The Manufacture of Gluten Feed. T. B. Wagner, New York City.

The Determination of Acidity in Cattle Feed. J. P. Street, New Haven, Conn.

Section C (food adulteration). (Annex Hall.)

Some Notes on the Lead Number of Maple Syrup. New York Food and Drug Inspection Laboratory.

Some Notes on the Analysis of Melado and Maple Sugars. New York Food and Drug Inspection Laboratory.

The Determination of Fusel Oil in Distilled Liquors. By A. S. Mitchell, St. Paul, Minn.

Results on Paprikas of Known Purity. New York Food and Drug Inspection Laboratory.

Determination of Starch in Cocoa and Cocoa Products. W. L. Dubois, Buffalo, N. Y.

Coal Tar Colors. C. B. Cochran, West Chester, Pa.

Determination of Sulphurous Acid and Sulphites. E. Gudeman, Chicago, Ill.

Examination of Oysters. W. D. Bigelow, Washington, D. C.

Moisture Determinations without Heat. P. F. Trowbridge, Columbia, Mo.

H. W. WILEY, *Secretary.*

The twenty-first annual convention of the Association of Official Agricultural Chemists, the program of which appears above, was one of the most enthusiastic and well attended in the history of the Association. Including members and guests about two hundred were in attendance. Besides the papers announced in the program, the following were read on Friday: Dr. B. J. Howard, on the Microchemistry of the Alkaloids; Mr. Emery, on Headache Powders; Dr. Salant, on Pharmacological Methods; Mr. C. E. Parker, on Drug Assaying; and Dr. H. H. Rusby on Drug Adulteration. In brief, the recommendations of Committee C were as follows: to appoint a committee of five to co-operate with the Bureau of Standards in drawing up an alcohol table; that methods for the determination of glycerol and total, fixed and volatile acids and coloring matters in wines be further studied; that the method for the determination of citral in extracts as presented be adopted as a provisional method; that the Baer and Neumann method for calcium sucrate in milk and cream be studied by the referee during the coming year; that the bichromate method for the determination of fusel oil in distilled spirits be made provisional; that the methods for fusel oil as given in Bulletin 107 be dropped; that the method for water-insoluble color as presented, also the Marsh test (quantitative) be adopted as provisional methods; that the methods for the determination of added oil in paprika be further studied; that the study of methods for separating proteins in meat be continued; that the determination of ammoniacal nitrogen with reduced pressure be further studied and compared with other methods; that the methods for separating the gluten proteins of flour be further studied; that methods for the detection of soaked peas and similar products be further studied; that further studies of meat proteins along present lines be continued; that the methods for caffeine in tea and coffee, and sugar in chocolate be further studied; that Doolittle and Woodruff's method for caffetannic acid be studied; that authentic samples of vegetable or natural colors used in food-stuffs be obtained and studied.

The report of the Joint Committee on Food Standards was read by the chairman, William Frear. In its main points the report was the same as that presented to the Mackinac meeting of the Association of State and National Food and Dairy Departments. Dr. Frear announced that the report would not be published in this year's Proceedings of the Association because of lack of authority on the part of the Secretary of Agriculture, but that the committee itself would publish it. The report of the Committee on Testing Chemical Reagents was delivered by Chairman L. F. Kebler and was of the nature of a report of progress.

The following officers were unanimously elected for the coming year: President, W. D. Bigelow; Vice-President, W. A. Withers; Secretary, H. W. Wiley; Members Executive Committee, E. F. Ladd and E. B. Holland. Among the social features that made the meeting enjoyable may be mentioned the informal receptions at the Cosmos Club and at the home of Dr. Bigelow.

THE SIXTIETH MEETING OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Baltimore, December 28, 1908, to January 2, 1909.

OFFICERS FOR THE BALTIMORE MEETING.

President.

Dr. T. C. Chamberlin, University of Chicago, Chicago, Ill.

Vice-Presidents.

A.—*Mathematics and Astronomy*—C. J. Keyser, Columbia University, New York.

B.—*Physics*—Karl E. Guthe, State University of Iowa, Iowa City, Iowa.

C.—*Chemistry*—Louis Kahlenberg, University of Wisconsin, Madison, Wis.

D.—*Mechanical Science and Engineering*—George F. Swain, Massachusetts Institute of Technology, Boston, Mass.

E.—*Geology and Geography*—Bailey Willis, U. S. Geological Survey, Washington, D. C.

F.—*Zoology*—C. J. Herrick, University of Chicago, Chicago, Ill.

G.—*Botany*—H. M. Richards, Columbia University, New York.

H.—*Anthropology and Psychology*—R. S. Woodworth, Columbia University, New York.

I.—*Social and Economic Science*—William Graham Sumner, Yale University, New Haven, Conn.

K.—*Physiology and Experimental Medicine*—William H. Howell, Johns Hopkins University, Baltimore, Md.

L.—*Education*—John Dewey, Columbia University, New York.

Permanent Secretary—L. O. Howard, Smithsonian Institution, Washington, D. C. *General Secretary*—Dr. J. Paul Goode, University of Chicago, Chicago, Ill. *Secretary of the Council*—Dr. D. C. Miller, Case School of Applied Science, Cleveland, O. *Treasurer*—R. S. Woodward, Carnegie Institution, Washington, D. C.

LOCAL EXECUTIVE COMMITTEE.

William H. Welch, M.D., *Chairman, Local Committee. Executive Committee*—Henry Barton Jacobs, M.D., *Chairman*; William J. A. Bliss, *Secretary*; Joseph S. Ames, William B. Clark, R. Brent Keyser, Eugene A. Noble, Ira Remsen, John E. Semmes, Francis A. Soper, Hugh H. Young.

The Sixtieth meeting of the American Association for the Advancement of Science, and the seventh of the "Convocation week" meetings, will be held in Baltimore, December 28, 1908, to January 2, 1909, at the invitation of Johns Hopkins University.

The opening session of the Association will be held at 10 o'clock A.M., on Monday, December 28th, in the McCoy Hall, Johns Hopkins University.

For all matters relating to the local arrangements, hotel and boarding house accommodations, not explained in the following pages, address Prof. Wm. J. A. Bliss, Secretary of the Local Executive Committee, A. A. A. S., Johns Hopkins University.

Section C.—Chemistry meets in affiliation with the American Chemical Society.

The meetings of the Association will be held in the buildings of Johns Hopkins University, Baltimore City College, Baltimore Medical College, The Woman's College and The Johns Hopkins Medical School.

The hotel headquarters will be at the Belvidere, Charles and Chase Sts.

The address of Vice-President Talbot before the Section of Chemistry will be delivered Tuesday, December 29th, at 2:30 P.M.

Full information in regard to the meeting can be obtained by addressing Secretary L. O. Howard, Smithsonian Institution, Washington, D. C.

NINETY-FIFTH GENERAL MEETING OF THE AMERICAN INSTITUTE OF MINING ENGINEERS.

The American Institute of Mining Engineers held its ninety-fifth general meeting at Chattanooga, Tenn., October 1st, 2nd and 3rd.

ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS' ASSOCIATION.

The American Leather Chemists' Association held its fifth annual meeting at Boston, Thursday, Friday and Saturday, November 12th, 13th and 14th.

TRADE AND INDUSTRIAL NOTES.

The hearings before the House Committee on Ways and Means in regards to the revision of the tariff, which is the subject to be taken up at the special session of congress to be called after March 4th next, began on Tuesday, Nov. 10th. The chairman of the committee is Hon. Sereno E. Payne of New York. Eighty-six paragraphs under schedule "A" of the Dingley tariff, embracing chemicals, oils and paints, were considered on Tuesday and Wednesday. Among those who appeared before the committee were John F. Queeny of St. Louis, Stewart Chaplain and John D. Pennock of Syracuse, N. Y., Dr. Springer of Cincinnati, George N. Brown of Philadelphia, James E. Davis of Detroit, Eugene Merz of New York, Frederick Schoelkoff of Buffalo, Arthur Somers of Brooklyn, M. E. Rhodes of St. Louis and S. M. Evans of North Carolina. The general sentiment of the speakers was in favor of the present duties and in some cases in favor of increased duties.

In the federal suit to dissolve the Standard Oil Co., held before Ex-Judge Franklin Ferris, John D. Rockefeller president of the company was on the witness stand November 18th to 25th.

The Greenawalt electrochlorination process will be tried on the ores of the Nevada Wonder mine at Wonder, Nev., following a successful demonstration by the Goldfield chlorination Reduction Works at Goldfield. It will be necessary to pipe water eight or nine miles to the mine.

A new fertilizer combination of international character with a capital of $50,000,000, is rumored. Incorporation will be under the New Jersey laws and Herman Schmidtman, of Germany, is mentioned for president. The Tennessee

Copper Co., through its great sulphuric acid plants at Ducktown, will be largely interested. The organization meetings will be held in New York.

The new plant of the Indiana Steel Company, at Gary, Indiana, will probably blow in the first of its sixteen five-hundred-ton blast furnaces in January. About 750,000 tons of ore are now in storage in the plant.

Consul-General William H. Michael, of Calcutta, reports as follows on the manufacture of castor oil in India:

There are two varieties of the castor-oil plant grown in India, the large and the small, and the mode of obtaining their respective oils may perhaps vary in different districts. One mode is to separate the seeds from the husks by children throwing them against a wall, then to bruise by tying up and beating them in a grass mat. In this condition they are put into a boiler and boiled until all the oil, which floats at the top, the refuse sinking to the bottom, is separated; it is then skimmed off and put away for use. The purest oil is said to be obtained by crushing the seeds in horsehair bags by the action of heavy iron beaters. As the oil oozes out it is caught in troughs and conveyed to receivers and bottled for use.

Castor oil is used medicinally, also for lamps in the East Indies, and the Chinese are said to have some mode of depriving it of its medicinal properties so as to render it suitable for culinary purposes. The plant is very extensively propagated by the Karnes to obtain the seeds to mix with their dyes and fix their colors. The oil obtained from the large-seeded variety is sometimes drawn cold, and its straw-colored specimens are scarcely distinguishable in quality from the oil of the small-seeded variety. It is, however, more usually extracted by heat, and forms the common lamp oil of the bazaar.

The total export of castor oil from Calcutta in 1907–8 was 1,362,842 gallons, valued at $666,665. The export of castor seed, or beans, amounted in value to only $63,000. (From *Daily Consular and Trade Report*, No 3325, Nov. 17, 1908)

On Sept. 8–12, 1908, at Geneva, Switzerland, was held the International Pure Food Congress, the so-called White Cross Congress, in which practically all the civilized nations participated.

Consul Samuel L. Gracey sends from Foochow the following note on the camphor industry of the Chinese Province of Foochow:

In the northern part of the Fuhkien Province among the thick forests there stand many camphor trees, some of which are over a thousand years old. In the former time, people did not know how to manufacture camphor and camphor oil. But in recent years they learned the method and found the traffic to be quite lucrative. The average quantity of camphor purchased and shipped from Kienning to Foochow each year by foreign and Chinese merchants is about 7,000 or 8,000 piculs (picul = $133\frac{1}{3}$ pounds) and that of the camphor oil is about 20,000 piculs. In the thirty-first and thirty-second years of Kuan-hsu the camphor dealers enjoyed a great profit, for the price of camphor was over $140 per picul, and that of the camphor oil was $60 per picul. But in the thirty-third year (last year) the price of camphor suddenly dropped to $80 per picul, and that of the camphor oil to $30 per picul. Dealers in camphor have all suffered great losses.

The Chemical Industry of Germany.

(From *Daily Consular and Trade Reports*, No. 3321, Nov. 3, 1908.)

Consul Thomas H. Norton makes the report from Chemnitz that at the recent annual session of the German Society for the Protection of the Interests of the Chemical Industry the reports made by the different branches showed that, with the exception of the manufacture of white lead and of other lead pigments, no serious effects had thus far resulted from the general business depression. The consul states that the report of the secretary gave the following outline of the growth of the industry during the year 1907:

The number of factories increased from 8,505 at the beginning of the year to 8,618 at its close. The number of operatives increased from 195,000 to 207,000. Their wages advanced at the same time from $49,266,000 to $54,740,000.

The joint stock undertakings, numbering 166, reported at the close of 1907 a total stock capital of $125,806,800, reserves of $41,316,800, and outstanding debts amounting to $22,514,800. They paid in dividends the sum of $19,444,600 on the entire capital. This is an increase of 0.38 per cent. on the rate for 1906. The profits vary greatly in the different branches. Of the 166 joint stock companies some 44 declared dividends ranging from 5 per cent. to nothing. The average rate of profit during 1907 for the entire industry was 10.73 per cent., an advance of 0.7 per cent. over the rate for 1906. The fluctuations in the average rate of profits in the chemical industry for the past eight years are shown by the following table, in which, for purpose of comparison, the rate of 1899, a year of exceptional prosperity, is placed at 100:

Year.	Rate.
1899	100.0
1900	91.2
1901	90.9
1902	87.8
1903	93.3
1904	98.7
1905	104 9
1906	111.5
1907	114.3

The outlook for a continuance of high profits is not considered as favorable, partly on account of recent tariff arrangements, and partly on account of the requirements of the new British patent law.

	Exports.		Imports.	
Preparations.	1907.	1908.	1907.	1908.
Acids, alkalies, salts, etc.	841,430.9	867,057.5	547,438.2	532,894.3
Colors and pigments	89,849.2	81,055 8	31,892.6	31 415.3
Varnishes, cements	1,789 8	1 914.7	1,568.2	1,191.5
Alcohol, ether, essential oils, aromatic compounds, cosmetics, perfumery, etc.	4,624.9	4,312.3	17,118.5	18,647.5
Artificial fertilizers	185,439.7	198,477.1	182,045.6	186,336.5
Explosives, matches	7,368 1	5,431 4	710.9	492.5
Other chemical and pharmaceutical preparations	12,873.3	12,465.5	19,648.8	21,798.5
Total	1,143,375.9	1,170,714.3	800,422.8	792,776.1

The customs statistics of the German Empire for the first half of 1908 give a most satisfactory showing for the com-

merce in chemicals. In comparison with the same period of 1907, there is a slight lessening of imports and a more marked increase in exports. The foregoing are the figures showing the German commerce in chemical products, colors, and pharmaceutical preparations for the first six months of the respective years, in metric tons of 2,205 pounds.

OFFICIAL REGULATIONS AND RULINGS.

Under date of Nov. 12th the Board of Food and Drug Inspection has issued notices of Judgment No. 22, Misbranding of Eggs; No. 23, Adulteration and Misbranding of Vinegar (Distilled vinegar artificially colored); and No. 24, Adulteration and Misbranding of Molasses (Admixture of glucose).

Under date of Oct. 30th the Board of Food and Drug Inspection has issued Food Inspection Decision No. 97, "Soaked Curd" Cheese, which states in effect that cheese made by soaking the curd at one stage of the process in cold water should be labeled "Soaked Curd Cheese."

Suit to enjoin the collector and the internal-revenue gaugers from marking rectified spirits "imitation whisky."—Decision of Judge Humphrey denying applicaton for preliminary injunction and sustaining the Government.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., October 9, 1908.

The appended decision in the case of Woolner & Co., *et al. v.* Percival G. Rennick, collector, *et al.* in the United States Circuit Court, Southern District of Illinois, is published for the information of all concerned.

JOHN G. CAPERS, *Commissioner.*

CIRCUIT COURT OF THE UNITED STATES, SOUTHERN DISTRICT OF ILLINOIS. NORTHERN DIVISION.

Woolner & Co., et al. v. *Percival G. Rennick, Collector, et al.*

BILL FOR INJUNCTION.

HUMPHREY, J.: The present application is for a preliminary injunction restraining certain officers and agents of the Internal Revenue Department from marking as "imitation whisky" potable distilled spirits from grain, of approximately 100 proof, which have been rectified so as to remove most of the fusel oil and aldehydes.

The complainants are engaged in the business of rectifying distilled spirits and the defendants are acting under printed regulation promulgated May 5, 1908, by the Commissioner of Internal Revenue, as follows:

4. Alcohol, commercial alcohol or high wines which have been manipulated by the aid of artificial flavors, colors or extracts, or otherwise, so as to resemble some particular kind of potable spirits, will be marked with the name of such spirits preceded by the word "imitation," as, for example, "imitation whisky."

The contention of complainants is:

First. That the regulation of May 5, 1908, is in violation of section 3449 of the Revised Statutes; that the product in question has, for a long time, been known to the trade as whisky; that the complainants as owners of same would be prohibited by Section 3449 from shipping it under any other name than whisky, "that being the name known to the trade," and therefore the Commissioner has no power to require a mark or brand which does not conform to the trade name.

Second. That the regulation is unreasonable and therefore illegal.

Third. That the injunction should issue under the rule known as balance of convenience.

Section 3449 is not in point. That section was passed by Congress to prevent frauds on the revenue and to assist revenue officers in discovering such frauds. It has no reference whatever to marks or brands placed upon packages by Government officers. The authorities are numerous and clear upon this question.

The argument on behalf of complainants that the new regulation is unreasonable, and therefore void, raises the real question in the case.

Powers requiring judgment and discretion when conferred by law upon executive officers must be exercised with reason. When found to be clearly reasonable, the courts will not interfere with officers acting under discretionary powers. When found to be clearly unreasonable such action will be held void.

That there is a product called *whisky*, and also a product called *imitation whisky* the law itself clearly contemplates, and Section 3244, in defining what is meant by the business of rectifying, denominates the maker of imitation whisky and other imitation liquors as a rectifier, and in passing upon the question whether the regulation of May 5, 1908, is reasonable or unreasonable it is necessary to determine the fact whether the Commissioner in that regulation has correctly defined an imitation whisky. That counsel have regarded this as the crucial question in the case, is evidenced by the fact that both parties have presented to the court numerous affidavits upon the subject. Complainants present 69 of such affidavits and the defendants a lesser number.

These affidavits are from rectifiers and distillers, members of the wholesale and retail liquor trade and scientists and chemists of high rank. They do not agree. Indeed, it may be said that some of them present diametrically opposite views more or less elaborately stated.

In brief, the affidavits for complainants tend to support the proposition that a distilled spirit from grain reduced by water to potable strength from which most of the fusel oil has been removed by rectification is whisky and that all distilled spirits from grain are "like substances," without reference to differences in their percentage of alcohol or of secondary products present therein.

The affidavits presented for defendants tend to support the view that whisky is a product made by the proper distilling of a fermented mash of grain with such care and at such low temperature as to retain the congeneric ingredients of the grain, aged under a normal temperature for not less than four years in charred oak casks. Thus broadly in statement do the chemists disagree. They are more or less persuasive to the court according to the soundness of scientific reasoning given in support of their statements.

The convincing weight of testimony on this subject, given by such men as Professors Frear of Pennsylvania, Scovill of Kentucky, Tolman and Adams of Washington, D. C., Shepard of South Dakota, Jenkins of Maine, Fischer of Wisconsin, and many other State analysts and chemists of repute, is to the effect that the neutral spirits reduced by

water to potable strength, from which most of the fusel oil has been removed, is not a like substance with whisky. Among the various reasons given for this conclusion are the following:

Whisky can be made from sound grain only, while neutral spirits can be made from moldy, heated, or unsound grain, or from various other substances, as fruits or vegetables.

Whisky is made at a lower temperature, say 150 to 155 degrees, so as to retain in the distillate the congeneric properties of the grain, the oil, the flavor, the higher alcohols and aldehydes, the esters, acids, and salts, which, when modified by further treatment, gives to whisky its desirable, potable character, a character which alcohol never possesses.

Neutral spirits are made at a very high temperature for the very purpose of carrying off, so far as possible to do so, every property of the distillate, except alcohol and water.

Whisky is aged and matured for not less than four years in charred oak barrels.

Neutral spirits require no aging, but may pass immediately into consumption.

The maturing of the product in charred barrels modifies and corrects its raw, biting taste. The action of the congeneric properties of the grain so retained in the liquor on each other and the action of the charred wood on all by the lapse of years results in a flavor, an aroma, a color, a blending of nherent constituents resulting in a beverage agreeable to the sight, to the smell, and to the taste.

In neutral spirits the name signifies the character. There is neither taste, smell, nor color, and no amount of aging in charred or uncharred barrels will change it without the addition of foreign matter.

The time required for maturing whisky resulting in a loss of perhaps 30 per cent. in quantity by evaporation and absorption adds greatly to the expense of making it over neutral spirits which require no maturing and suffer no loss of quantity thereby.

The record also shows that diluted spirits treated with artificial coloring matter and essences are not sold to the trade as such, but are always presented under such labels, terms, and descriptions as impart age and maturity, and which the consumer identifies with the genuine product whisky. The regulation is in all respects reasonable and is therefore legal.

The fact that this practice had, to some extent, prevailed for many years does not show in the complainants any right which the court should protect. It shows rather that the Commissioner of Internal Revenue has been tardy in promulgating a regulation which he had legal power to enforce, even before Congress gave emphasis to the subject by the enactment of the food and drugs act.

The preliminary injunction will be denied.

Note.—United States Attorney Northcott writes to the Commissioner as follows:

I notice that some of the newspapers construe the decision of Judge Humphrey in the case of Woolner Distilling Company as a criticism upon your Department.

In a conversation with Judge Humphrey, he authorizes me to say that no criticism on your Department was intended by the decision, but, on the contrary, the Department was sustained on every proposition.

(T. D. 1427) *Marking Spirits.* Application for an injunction *pendente lite* to enjoin the collector of internal revenue from carrying out Circular 723 of May 5, 1908, issued in conformity with the direction of the President to the Secretary of Agriculture for the enforcement of the pure-food act with reference to the marking and branding of the products of distilleries as "alcohol" instead of spirits.—Decision of the United States circuit court, northern district of California, denying motion for injunction.

(T. D. 29312—G. A. 6821) *Cutch.* "Cutch made from the mangrove tree which is so treated chemically in the processes of manufacture, or after manufacture, as to reduce the coloring properties thereof and make it suitable for use in tanning leather, is known in trade and commerce as cutch and is entitled to classification as such under paragraph 542, tariff act of 1897."

This decision is interesting, aside from the points involved, for the opinions expressed in regard to the testimony of chemical experts and the setting aside of the expert testimony in favor of that of "practical" men.—Ed.

(T. D. 29330) *Drawback on flavoring extracts.*

(T. D. 29331) *Drawback on maple sirup.*

(T. D. 29339) No. 19886.—Coal-Tar Preparation—Toluidin M.—Protest 310767 of Geisenheimer & Co. (New York). Opinion by Chamberlain, G. A.

The merchandise consisted of toluidin M, held dutiable under paragraph 15, tariff act of 1897, relating to coal-tar preparations. The only question was whether it was a coal-tar product not a color or dye and not medicinal, as claimed by the importers. Protest sustained.

(T. D. 29339) No. 19913.—Alizarin Rubinole R. Powder. Protest 318047 of Farbenfabriken of Elberfeld Company (New York). Opinion by Chamberlain, G. A.

So-called alizarin rubinole R powder, classified as a coal-tar color under paragraph 415, tariff act of 1897, was claimed to be free of duty under paragraph 469 as a dye derived from alizarin or anthracene.

(T. D. 29339) No. 19944.—Annatto Butter Color.—Protest 302283 of Minnesota Creamery Supply Company (St. Paul).

So-called "annatto butter color," classified as an unenumerated manufactured article under Section 6, tariff act of 1897, was claimed to be free of duty under paragraph 475, relating to "annatto, roucou, rocoa, or orleans, and all extracts of." Protest overruled.

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EDITORIALS.

NATURAL RESOURCES AND MANUFACTURE.

We have, as a nation, acquired the habit of being vastly satisfied with what we have accomplished. We marvel at our enterprise in scraping iron ore from the earth's surface by steam shovels, in growing wheat on virgin soil, in stripping great areas of primeval forest, in burning natural gas and allowing petroleum to spout from the ground. Even Germany acknowledges that she cannot compete with us in raising cotton, and we cut more ice in a month in the single state of Maine than all the Pictet machines in France can turn out in a year. We control the copper market of the world—because we have the copper. If you want cheap sulphur, you must come to us, we pump it from the ground. We develop great centres of power distribution because our rivers run so fast down hill.

To these vast resources we have, indeed, brought a native energy, an unusual capacity for organization, and a genius for mechanical affairs. What we do, we do on a great scale, but we often do it very badly. It is quite time for us to pause in our self-congratulation long enough to inquire whether the things we are doing cannot be better done, whether, in fact, other nations have not developed and put to use much better methods, which, given equal opportunity, would put our own performance to the blush.

Although the resources of a country form the basis of its prosperity, this is, nevertheless, determined in the long run by the manner in which these resources are utilized, or, in other words, by the industrial efficiency of the means and methods of production. We have developed great transportation systems, we handle raw material on a titanic scale, we have applied machinery to the addressing of our letters and the sticking of the stamps, but it remains true, none the less, that with a few conspicuous exceptions, our manufacturing operations are carried forward in trustful ignorance and disregard of many of the factors upon which real industrial efficiency depends. This is shown in the stupendous waste which accompanies the first crude preparation of the raw material; it is shown in the general absence of a true selective economy in the apportionment of that raw material among the different industries, and it is shown again, and yet again, in the losses which attend nearly every step in the progress of the raw material toward the finished product. One need only refer to the wastes which attend lumbering, or to the growing of flax for seed, the making of coke in bee-hive ovens, and the failure to utilize the casein of skim milk as a high-grade food product, to realize vaguely something of what these initial losses are. The absence of proper selective economy in the adaptation of raw material to use is everywhere, as when our railroads use untreated ties and poles, when coal-tar is burned as fuel, crystal alum used for purifying water, or valuable publications printed on ground-wood

papers. We are still polluting our streams with wool grease, still wondering whether we can make alcohol from waste molasses, still buying coal without reference to heating power, and paying 65 cents a gallon for cylinder oil.

When wastes so obvious and so easily remedied are everywhere taking heavy toll of our manufacturers, it is not surprising that in all lines of productive effort subtle and elusive problems present themselves and still further lower our industrial efficiency. Steel rails break by thousands, trolley wires snap, boilers corrode, milk-cans rust, unsightly bloom appears on leather, cloth is stained or tendered, paints fail to protect the metal underneath. In a large proportion of cases, those who are confronted by the problem, have neither the time, the training, nor the equipment required for its solution, and yet such problems and thousands of others far more complex upon their face must be solved if our industrial efficiency is to be brought to its proper level.

No one at all conversant with the facts can doubt that our industrial salvation must be found in a closer alliance and co-operation between the scientific worker and the actual agencies of production. Such co-operation exists, as we are all beginning to learn, in Germany, and its results are evident throughout the world in the tremendous expansion of German industry.

No one at all familiar with the conditions under which thousands of American manufacturers are working can fail to realize the unique and fruitful opportunity which spreads out before the Laboratory nor can they doubt that the funds for its development will be forthcoming. Within the last few years there has opened out to the worker in applied chemistry a new horizon with a sweep so broad that it is seen to include far more than the mere material gains which come from more efficient effort. It has come to be recognized that the lives of great masses of the community are constricted and confined because our industrial efficiency as a people is still far below what it ought to be. In this stage of our industrial development no agency is more directly available for increasing this efficiency than that afforded by chemistry as applied to industry. Every waste that is prevented or turned to profit, every specification which gives a better control of raw material, every problem solved, and every more effective process which is developed, makes for better living in the material sense and for more wholesome living in the higher sense. It means much to the material and more to the higher well-being of German workmen that their nation now controls the coal-tar industries, the manufacture of fine chemicals, and the markets of the world in many other lines, chiefly as the result of the application of the scientific method to the problems of production. The general application of these methods will mean even more to our own country.

ARTHUR D. LITTLE.

STANDARDIZED SAMPLES.

IT is not at all surprising that the subject of accuracy in chemical analysis is constantly undergoing discussion. As so much depends upon the analysts' work, both in settlements for materials bought and sold and in the control of works' processes, it would seem that almost anything within reason ought to be done to insure the accuracy of his results. At frequent intervals, papers appear dealing with the preparatory and technical training of the chemist, the formation of an Institute of Chemistry, the use of reagents of guaranteed composition, the calibration of weights and measuring instruments, and the development of new or improved analytical processes. In addition, much effort is expended in the endeavor to obtain uniform or official methods of analysis for use in certain industries.

Experience has shown that the coöperative analysis of a given sample by a number of chemists serves only to call attention to the probable variations in results obtainable by men who strive for accuracy, but who work under such different conditions that non-concordant determinations are almost inevitable. As a means for developing better, and perhaps uniform, methods of analysis, it would be desirable to have a limited number of well trained men work out what they consider the best method available, with one or more optional methods in addition, and then put their analytical "scheme," together with carefully standardized samples, in the hands of chemists at large. An analyst of any degree of experience or skill could then practice with the standardized sample until he had perfected himself in the proposed method. This way of working brings splendid results with students of quantitative analysis—why should it not be equally successful with chemists of greater maturity?

The use of a standardized sample as a check

upon different chemists using the same method of analysis, upon the same chemist using different methods of analysis, and as an umpire sample in cases of dispute between analysts, will suggest themselves immediately. As a check upon original methods of analysis, enabling the operator to determine with comparatively little effort the applicability and accuracy of his method, standardized samples are well worth their cost. In cases of disputed analytical results it would doubtless lead to a better agreement were both parties to analyze a standardized sample of the same kind of material and discover which is at fault, rather than go through the usual process of submitting the original sample to a third party—who may be no more capable than the contending analysts—for an umpire analysis.

Some ten or more years ago, a foundrymen's association did a real service to the chemists of the iron and steel industry by preparing, with great care, a set of iron samples, having them analyzed by three or four chemists of recognized ability, and then selling these standardized samples at a reasonable price. In a recent number of *Science* (October 2, 1908), Launcelot Andrews proposed that similar work, but on a much larger scale, be undertaken by the Bureau of Standards. He would have the Bureau furnish both substances used in the preparation of standard solutions and samples of raw materials or finished products.

The Bureau of Standards has already prepared a number of standardized iron and steel samples which it sells at fixed prices (THIS JOURNAL, page 41) and has under consideration the preparation of special steel samples. The National Fertilizer Association has prepared and distributed four samples of phosphate rock which may now be considered to be standardized. The Committee on Analysis of Fats, Soaps and Glycerine, of the American Chemical Society, has prepared and distributed samples of the products which it has under consideration and these after analysis by experts may be considered as standardized. Thus, even up to the present time, some work on the preparation of standardized samples has been done.

Even before Andrews' paper appeared, the thought had occurred to some members of the American Chemical Society that this was a field which the Division of Industrial and Engineering Chemistry might do yeomen's service. With a membership made up of representatives of almost all the chemical industries carried on in this country, with three publications of large circulation at its disposal, and with the enthusiasm of youth to enable it to carry out successfully big undertakings, the Division ought to be in a position to prepare, standardize and distribute samples of materials for which there may be a demand. The expenses involved could be defrayed from the sale of the samples. Is the suggestion not well worth considering?

W. C. EBAUGH.

THE ROAD PROBLEM AND THE CHEMICAL ENGINEER.

ONE of the most important problems of the day, which requires the consideration of those who are in charge of the construction and maintenance of our highways, is that of how to meet the destructive effect of modern motor traffic. It has become one of such prominence that an International Road Congress was held in Paris in October last, on the initiative of the French Government, to consider the subject, at which twenty-five nations were represented by nearly twenty-three hundred delegates and individuals. It was surprising to find, as a result of the Congress, how little the chemical engineer and chemist have been utilized abroad in solving the problem, and that America is far in advance of other nations in this respect. Nothing has been done abroad which in any way corresponds to the investigations carried out in the laboratory of the Office of Public Roads of the United States Department of Agriculture, and it is rumored that an effort has been made to interest it in an examination of the stone in use in the construction of roads in Great Britain. For at least twenty years, American chemists have been engaged in the study of the native bitumens in the light of their application to the construction of pavements and roads, and it is interesting to note that the appreciation of their usefulness in this work has grown to such an extent that the services of a very considerable number are employed by municipalities and others in regulating the construction of pavements and the materials employed therein, as well as in investigating the character of the bitumens available for rendering macadam roadways more resistant to the attacks of motor travel. The field of usefulness is constantly increasing and widening, and the opportunity for accomplishing something by chemists in aiding to solve the road problem is large.

CLIFFORD RICHARDSON.

THE ELECTRIC STEEL FURNACE.

It is probable that portions of the testimony recently given by Mr. Charles M. Schwab before the Ways and Means Committee at Washington will be very generally considered by those interested in iron and steel. Mr. Schwab pointed out the superiority of open-hearth steel, but affirmed the certainty of his opinion that within ten years, these furnaces would become practically useless because of the development of the electric steel furnaces. Naturally, much weight is attached to the evidence of such a witness before such a tribunal. The conditions may well warrant his conclusion. It has been recognized that there is sufficient difference between the value of the iron and other components of a high-grade tool steel and the prevailing price of the combination plus necessary labor, to pay for any electrical energy likely to be used in the electrical processes. There seems to be an essential disparity between the prices of a cent a pound for 97 per cent. iron and fifty cents a pound for 99 per cent. iron. Probably this difference, which is due to conditions inherent in crucible-steel manufacture, will be the first to attract the attention of the steel producers to the electric furnace. It was pointed out by Mr. Schwab that the electric furnace could be used for improving the quality of the lower grades of steel, such as rails. Here there does not seem to be a great chance for saving in cost of production of identical product. The refining of already molten open-hearth steel by treatment under the conditions supplied by the electric furnace (high temperature, slag- and composition-control, and reducing atmosphere) will doubtless not exceed a very few dollars a ton, if indeed it is not less than one dollar per ton.

Judging by the magnitude of the past fluctuations in prices of rail and structural steel, it would seem a small matter if the cost of production were even doubled, provided the quality was essentially improved. No one of our useful metals seems likely to be soon reduced cent per cent. by any conceivable change in the cost of production. Therefore, the premonitions of great reduction in cost of tool steel are particularly interesting. The open-hearth production is nearly one hundred times as great as the crucible steel production, so that any proportionately smaller ripple of improvement on the surface will represent a much greater real commercial wave of advance.

W. R. Whitney.

AN AMERICAN INSTITUTE OF CHEMISTRY.

There is a real need for an American Institute of Chemistry. In any given trade or profession, it is impossible for any body to accurately estimate the fitness or capability of any particular member of it, except another and experienced member of that same trade or profession. All through human effort it is the case that it takes a fellow craftsman to judge intelligently a worker's efforts. Therefore, to safeguard employers, and at the same time help deserving workers, the principle of the proposed Institute of Chemistry is a principle that should be applied in every department of industrial activity, and doubtless in time will be so applied.

As a matter of fact, it is to-day applied in many lines: medicine, law, dentistry, civil and mining engineering, etc. The doctor's diploma for instance gives from experienced and able men in the same profession, assurance to the public that the holder has a good knowledge of the rudiments of his business. It serves exactly the same purpose and is based on exactly the same principle as a certificate later on from an Institute of Medicine, supposing there was such a thing. And it would be well if there were such a thing, because the original diploma certifies merely to the rudiments and gives no hint with regard to after-standing. Take two graduates in medicine and in ten years the one may far outstrip the other in knowledge and efficiency. Yet, as far as the information conveyed by the original diploma is concerned, they are still on the same level. But if an "Institute" would be a good thing in the medical profession, where there is always a diploma to start with, far more would it be a good thing in the chemical profession where there is no diploma at all—or rather, no diploma that corresponds to the medical diploma. The medical diploma certifies that the holder has spent a certain number of years in the exclusive study of his profession. The chemist's, on the contrary, testifies that he has not spent these years in the exclusive study of his profession, but has spent them in the study of science in general with chemistry merely as an appropriate (though it is true, an exaggerated) incident.

In other words, the chemist's degree certifies to employers merely that the holder is not a chemist but a general scientist who has made a specialty of chemistry. This is much but leaves plenty of room for the Ph.D. degree and the M.S. degree, and these latter in their turn, though far above the proposed Institute certificate in dignity and

importance, still leave room for the Institute certificate. Although the need for something like the proposed Institute is a need that exists in every business high and low, yet there is no business where it is needed so badly as in analytical chemistry, for there is no other business where the employer is more absolutely incapable of judging for himself whether or not his employee is capable and deserving, and as matters now stand, the analytical chemist must rely for advancement and appreciation rather upon his engaging personal qualities, if he has any, than upon his professional capabilities. In fact, it is hardly too much to say that in the iron trade at least, the latter are a bar rather than a help to advancement, if the employer has no outside sources of information about his chemist, for if the chemist has professional capability, and professional pride, in his work, he will rarely succeed in satisfying his employers in the matters of speed and output of work. A far closer approach to the steel man's ideal in these respects would be made by a laboratory boy ignorant of chemistry, and innocent of conscientiousness, and it is by no means a reckless or random statement that in the iron trade, the better the chemist, the lower his employer's opinion of him, if the employer has nothing to guide him but his own impressions. With conditions as they are to-day, with employers almost unanimous in the conviction that chemical analysis is quick and easy work, and with the gr at majority of chemists seeking to humor and adapt themselves to this foolish misconception, rather than to combat and correct it, the lot of the conscientious analyst would be hard indeed without the testimony and the support of college degrees and other honors that he may succeed in gaining. Let us have more on the same principle as the College degree!

The College degree is the first thing; it is most important but it is not enough. It certifies to college study. But study does not end with the closing exercises of college. At that point it may be said to begin. What have we now to certify to this real serious life study that begins only as college ends? We have the Ph.D. degree and it is a glorious thing. But that it leaves nothing more to be desired, and that its testimony represents the acme of human effort, and human achievement, we have to deny. Admirable as is the Ph.D. degree, and of more dignity and importance than anything else in the same line, still there is room for more in the same line. The question confronting the chemical profession in America is this: Since the College degree is a good thing, shall we develop the underlying principle of it further, or shall we stop there and be content?

George Auchy.

ORIGINAL ARTICLES.

[Contribution from the Laboratory of the Fuel Engineering Company, Chicago, Illinois.]

THE AMOUNT OF INERT VOLATILE MATTER IN THE MINERAL CONSTITUENTS OF COAL.

By W. Brinsmaid.

Received November 5, 1908.

Chemists working on the analysis of coal have long known that the non-volatile mineral matter that they weighed and called ash did not truly represent the weight of the inorganic matter, when in its original form in the unburned coal.

They have also known some, if not all, of the sources of error but have not been able to calculate the amount.

The combined water in fire clay and gypsum, and the presence of carbonates that give off carbon dioxide on heating may be mentioned as probably the principal sources of error in weighing an ash correctly.

Pyrite also loses weight when burned to ferric oxide and is thus a source of loss. In case the amount of pyrite present in the coal were known, then the addition of five-eighths the weight of its sulphur content to the ash would correct for this loss. Unlike the other cases, however, this loss is accompanied by combustion and develops some heat. We might, therefore, call the iron in the pyrite inert matter and the sulphur a combustible and deduct the weight of the oxygen that unites with the iron, when the pyrite is burned to iron oxide. However, the determination of the amount of pyrite in coal is attended with some difficulty. The usual method has been to calculate the pyrite from either the iron present or from the total sulphur.

As coal may have iron present in other forms than pyrite, and generally has organic sulphur and sometimes gypsum present, it can readily be seen that any determination of pyrite in coal that is based on total iron or total sulphur may be the reverse of accurate.

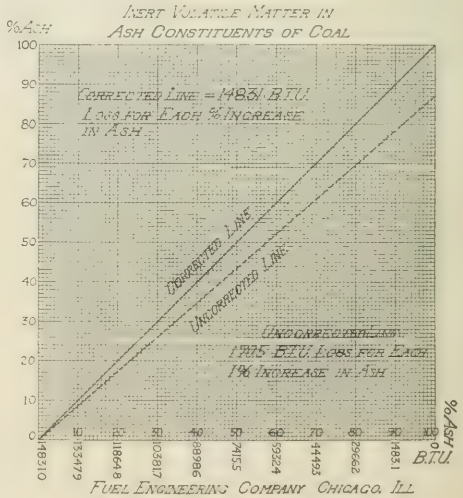
In speaking of the determination of oxygen by difference in ultimate analysis of coal, Prof. Lord

says:[1] "The result so obtained is always inaccurate, the error increasing with the percentages of the ash and sulphur. The weight of the ash does not represent that of the mineral matter in the coal, the pyrite in the coal being burned to Fe_2O_3, and the sulphur passing off as SO_2. Thus 4 of sulphur in 2 FeS_2 (pyrite) is replaced by 3 of oxygen in Fe_2O_3, and the loss of weight is equal to five-eighths of the sulphur. For this reason many chemists use five-eighths sulphur instead of sulphur in the determination of oxygen by difference. As coals contain sulphur in other forms than FeS_2 and also frequently other compounds that lose weight on burning, such as $FeCO_3$ and $CaCO_3$, it is doubtful whether the results obtained in this way are any better than those given by the simple formula first given."

In fact a calculated correction made in this way may be a greater source of error than the absence of any such correction. These various losses in weight, of the mineral constitutents of coal, are an important factor in some calculations and vary considerably in different coals. I will endeavor to show how we can arrive at the sum total of these losses, although we cannot tell of what they consist or at present make any special corrections.

Sometime ago it became necessary for the laboratory of the Fuel Engineering Company to get out a set of tables for various coals, by which one coal could be compared with another, and their relative value shown in heat units. Under the advice of Mr. E. H. Taylor the following method was worked out in the laboratory. A sample of coal was taken and the whole sample (which was usually about thirty pounds) was turned on to a clean table.

There were then picked out by hand some of the very best pieces in the whole sample. These were laid aside and another sample was picked by hand in such a way that it would have about a 20 per cent. ash. Care was used to see that this sample had all its ash constituents present in the proportion natural to the sample. This could be done by proper crushing and mixing and was necessary for the reason that there were often present pieces of both the roof and bottom which varied widely in their character. We had then two samples of coal, one of which was the very best coal that could possibly be gotten from that mine in a commercial way, and the other representing the same coal but very high in ash. These two samples were then ground to pass a 100-mesh sieve and the ash was determined on each sample. From the ash of these two samples there were calculated four more coals to make a series having per cents. of ash increasing in regular order, and these were then made up from mixtures of the low and high ash samples. For instance, if we found our low ash coal to be 5 per cent. ash and the high ash coal to be 20 per cent. ash, four mixtures of these two coals would be made having respectively 8, 11, 14 and 17 per cent. ash. Thus we got samples of a certain coal having 5, 8, 11, 14, 17 and 20 per cent. ash. There is nothing artificial about this set of coals but on the contrary it is all the natural coal and everything is in its proper proportion. This set of six coals was then carefully run in duplicate in a Mahler oxygen calorimeter and the ash was also run in duplicate. These results were then plotted on cross-section paper, and if the work had been carefully done the result was a straight line. The line, however, showed a peculiarity.



As an example I will use an Illinois coal that is quite common in the Chicago market. The line of this coal shows that it has at

5 per cent. Ash	—13978.5	British	Thermal	Units
4 per cent	" —14149.0	"	"	"
3 per cent	" —14319.5	"	"	"
2 per cent	" —14490.0	"	"	"
1 per cent	" —14660.5	"	"	"
0 per cent	" —14831.0	"	"	" or pure coal.

[1] "Notes on Metallurgical Analysis," N. W. Lord, page 170.

This shows that each addition of 1 per cent. ash means a loss of 170.5 British Thermal Units. If the line is carried along through increasing per cents. of ash it will be found that at 87 per cent. ash the B. T. U. are used up. We can also say that if each 1 per cent. of ash represents the loss of 170.5 B. T. U. (which the line shows to be the case), then the loss of 100 per cent. ash or the pure coal would be 100 × 170.5 B. T. U. or 17050 B. T. U. However, we have already seen that our pure coal is 14831 B. T. U. Now as to this difference. We rely much on the accuracy of the Mahler oxygen calorimeter.

Much use of the instrument has proved that it is accurate and reliable, and if properly handled will give close and concordant results. We, therefore, conclude from this that our determinations of the B. T. U. are correct and that the discrepancy is caused by the ash, and as our line shows that we have not sufficient B. T. U. to carry the line to 100 per cent. ash, then also we conclude that what we have been weighing and calling 1 per cent. ash represents matter that in the original coal weighed more than 1 per cent.

This being so, then the only correct figure we have in our table is 0 per cent. ash or pure coal, as this is the only figure in which all errors, due to loss of volatile non-combustible matter in the ash constituents, are eliminated. Our figure for pure coal then being 14,831 B. T. U., our factor of loss for each 1 per cent. ash will be 148.31 B. T. U. instead of 170.5. Our line having used up all B. T. U. at 87 per cent. ash shows us that we have lost 13/100 of our total ash, or in other words, each 1 per cent. ash that we have weighed as such really represented 1.13 per cent. inert matter in the original coal, of which amount 0.13 per cent. was volatile and non-combustible. While we have good grounds for stating the amount by weight of this volatile non-combustible matter in the ash constituents, we have nothing to show of what it is composed, and so we are as far as ever from this very desirable and interesting point.

This loss, of which no account has been taken, throws some light on certain discrepancies which have never been explained. Much work has been done on certain lines in the endeavor to get a basis on which coals might be compared. The pure coal basis has been used, with and without a correction for pyrite.

Ash- and moisture-free coal has usually been called pure coal. Now pure coal must necessarily be only one thing for a certain coal and should be the same figure when calculated from any per cent. of ash. The fact is, however, that it varied with each difference in the ash, and the same coal from the same mine would give as many different figures for pure coal as there were different per cents. of ash in the different samples.

As stated in the first part of this article, the correction for pyrite in the coal based on the total iron or total sulphur may in some cases be misleading. A glance at our original line with uncorrected ash will show the cause of some errors. As the error in the ash increases regularly for each 1 per cent. of ash as weighed, then the error in a 10 per cent. ash would be twice as great as in a 5 per cent. ash, and the error not being recognized as present, they would never figure back to a common basis.

This method has never proved of any practical value and has been generally discarded. It has also been stated that in calculating this pure coal, a correction should be made for water of constitution in the mineral constituents. While this is a fact commonly recognized, still we are as yet unable to make such a determination. Until we are able to determine this point with a reasonable degree of accuracy, there is not much that we can say in regard to it.

In the ultimate analysis of coal there are three of the principal determinations that we know may be in error. Carbonates if present will give up carbon dioxide and this will be calculated as carbon, so this determination will be too high. Combined water will be calculated to hydrogen and cause this determination to be also too high. Oxygen being determined by difference is a very uncertain figure as all the errors may effect it. Having no ultimate analysis on this particular coal that I am using as an example, I will take the average oxygen and ash of thirty Illinois coals on which the ultimate analysis has been run, to show what difference a corrected ash would make in the oxygen figure alone. The average ash is 14 per cent. and the average oxygen figure is 8.75 per cent.

In the coal taken as an example when 1 per cent. of ash as weighed equals 1.13 per cent. ash in the coal, the corrected ash would be 15.82, thus lowering the oxygen figure from 8.75 per cent. to 6.93 per cent. Such corrections as this show why at times heat values calculated by Dulong and Pettit's formula vary so widely from the heat values as determined by the oxygen calorimeter.

We find that coals vary, as we would naturally expect, in the amount of this volatile non-combustible that is included in the mineral constituents. On the few coals that have been calculated in this manner we find the largest amount to be as in the table used as an example. In this table each 1 per cent. of ash as weighed equals 1.13 per cent. of ash in the coal unburned. The smallest amount found, 1 per cent. ash as weighed, equals 1.067 per cent. ash in the unburned coal.

It is very probable that further work along this line will show a wider variation than is given above.

THE STABILITY OF ROSIN AT SLIGHTLY ELEVATED TEMPERATURES.

By Chas. H. Herty and W. S. Dickson.

Received November 16, 1908.

On heating American rosin to 120°–140° C. in a current of air freed from carbon dioxide, Schwalbe[1] obtained a copious precipitate of barium carbonate by conducting the gases from the flask in which the rosin was heated into a solution of barium hydroxide. He interpreted this as evidence of the decomposition of the abietic acid in the rosin with consequent formation of the hydrocarbon abietene, and pointed out the effect such a decomposition must have upon the melting point and saponification number of rosin.

From evidence obtained during the course of another investigation we were inclined to doubt the accuracy of Schwalbe's interpretation. Accordingly the following investigation was undertaken, the results of which show that rosin which has not been long exposed to the oxygen of the atmosphere can be heated indefinitely at 140° without showing any evidence of the formation of carbon dioxide, provided oxygen and moisture are excluded from the flask in which the rosin is heated.

EXPERIMENTAL.

At the outset Schwalbe's experiment was repeated. For heating the rosin a 200 cc. Erlenmeyer flask was placed in a beaker containing cottonseed oil. The air entering the flask was freed from carbon dioxide by being drawn through three wash bottles filled with a strong solution of sodium hydroxide. After leaving the flask the air was passed through a test tube half filled with freshly filtered barium hydroxide solution. Another wash bottle containing a solution of sodium hydroxide was placed between the barium hydroxide tube and the aspirator, a suction pump. A blank experiment with this apparatus showed no precipitation of barium carbonate after drawing air through for one hour. A repetition of Schwalbe's experiment showed a copious precipitation of barium carbonate.

The possibility that this evolution of carbon dioxide might be due to the action of the oxygen of the air upon the heated rosin, aided by the presence of slight traces of spirits of turpentine in the rosin, led to a repetition of the experiment using spirits of turpentine alone instead of rosin. With a specimen of old spirits of turpentine an even heavier precipitation of barium carbonate occurred than with rosin. No question of the splitting off of a carboxyl group could arise here. A specimen of freshly distilled turpentine showed also a precipitation of barium carbonate, but not so marked as with the old specimen.

Having proved that the spirits of turpentine alone was capable of giving the precipitation observed by Schwalbe, a current of steam was passed through molten rosin for eight hours in order to completely remove all spirits of turpentine. Repeating Schwalbe's experiment with this rosin the precipitation was still observed. Evidently the presence of slight traces of spirits of turpentine was not alone responsible for the precipitation observed.

It remained therefore to determine the possible influence of oxygen and of moisture on the formation of carbon dioxide from the molten rosin. Accordingly, the current of air drawn through the flask was freed first from carbon dioxide by sodium hydroxide, then dried by passing through sulphuric acid. A marked precipitation of barium carbonate was again observed. Then moist nitrogen was substituted for air. The nitrogen was prepared by drawing air through three wash bottles filled with an alkaline solution of pyrogallic acid. Again a precipitation of barium carbonate occurred. Finally a current of dry nitrogen was drawn through the flask and after all air had been expelled the rosin was heated to 140° and kept at this temperature for seven hours without the slightest precipitation in the tube containing barium hydroxide.

The above experiments were carried out on a specimen of freshly distilled rosin from the oleoresin of *Pinus heterophylla* (Cuban Pine). This

[1] Zeit. angew. Chem. **18**, 1852.

suggested the possibility that Schwalbe had used a rosin from the oleoresin of *Pinus palustris* (Longleaf Pine). Accordingly a fresh specimen of rosin was prepared from the oleoresin collected from a single tree of this species. On heating the rosin in dry nitrogen to 140°, again no trace of precipitation was noticeable.

Finally Schwalbe states that his experiment was made upon a sample of commercial American rosin. On heating such a sample in dry nitrogen we found an abundant precipitation of barium carbonate.

Four factors therefore may have entered into the formation of the carbon dioxide observed in Schwalbe's experiment: first, traces of spirits of turpentine in the rosin; second, moisture; third, oxygen in the air conducted through the flask; and, fourth, oxygen absorbed either by the oleoresin previous to distillation or by the rosin on standing in the air. The explanation of a probable splitting off of a carboxyl group is demonstrated to be erroneous by using a sample of rosin recently distilled from a fresh specimen of the oleoresin and heating in a current of dry nitrogen.

And yet, paradoxical as it may at first appear, Schwalbe's explanation is even more than true; not in regard to "American rosin," but as applied to the acids of the oleoresin from which rosin is prepared. In order to avoid any elevation of temperature in the preparation of these acids, freed from the other constituents of the oleoresin, a specimen of the oleoresin of *Pinus heterophylla* was dissolved in ether. From this ethereal solution the potassium salts of the acids were precipitated by addition of a saturated water solution of potassium hydroxide. The crystal broth was mixed with glass wool to render it more permeable to an extractive, then thoroughly extracted with ether in a Soxhlet extractor. After removal of the last traces of ether the salts were dissolved in water, the solution acidified with dilute hydrochloric acid, and the precipitated acids washed and dried. On heating a specimen of these acids in the apparatus described above in a current of dry nitrogen the mass melted at 65°–70°, immediately evolution of carbon dioxide began as shown by the escape of gas bubbles from the molten mass, and the heavy precipitation of barium carbonate.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C.

SOIL ACIDITY IN ITS RELATION TO LACK OF AVAILABLE PHOSPHATES.

SECOND PAPER.

BY C. W. STODDART.

Received October 20, 1908.

In a previous article upon this subject[1] it was shown that acid soils need a phosphate fertilizer. This fact was noted not only in the work of other men on acid soils but also from field and plant-house fertilizer tests on numerous Wisconsin soils. Since the publication of the preliminary paper further tests have confirmed that statement, with one exception, and that, where a test was made on an acid virgin soil in which no fertilizer need was indicated, as might be expected.

Although there is phosphoric acid present in these soils in sufficient quantity for many crops, it is not available, and hence the soils need phosphate fertilizers. That acid soils do lack available phosphates is a fact, but the question now arises as to a causal relation, if any, between the two conditions; that is, whether lack of available phosphates is due to the acid condition of the soil. If this is true, it may be explained as follows: The soil acids act upon the readily available phosphates, such as the calcium phosphates, at a more rapid rate than the normal, neutral, or alkaline soil moisture, and when once in solution these phosphates are readily washed out by heavy rains, or are fixed by iron and aluminum compounds—that is, are precipitated and rendered unavailable as insoluble iron and aluminum phosphates. When there is sufficient lime in the soil to maintain the phosphoric acid in the form of calcium phosphate, the plant is able to obtain enough phosphorus for its use, since calcium phosphate is soluble enough to supply the needs of the growing crop. If it can be shown by chemical analysis that acid soils contain more iron and aluminum phosphates and less calcium phosphate than do non-acid soils, and particularly if they contain a greater ratio of iron and aluminum phosphates to calcium phosphate, there is evidence in favor of causal relationship between acid soils and lack of available phosphates.

In order to test this matter it is necessary to find some solvent which will extract the iron and aluminum phosphates and not the calcium phosphate, and vice versa. In selecting solvents which will extract these minerals separately from the soil

[1] Whitson and Stoddart, *J. Am. Chem. Soc.*, **29**, 757.

it is advisable to try them first on pure minerals, although it is well recognized that the action of any solvent on a pure mineral may not be the same on that mineral when it occurs in the soil, since the soil is a complex mixture of various minerals in different stages of weathering, and of organic matter in all forms of decomposition. It is commonly assumed that the principal phosphate minerals occurring in the soils are apatite (calcium phosphate), dufrenite (basic iron phosphate), and wavellite (basic aluminum phosphate). The mineral samples tested with the various solvents contained, in the case of apatite, 39.7 per cent. phosphoric anhydride; of dufrenite, 19.6 per cent.; of wavellite, 19.5 per cent. Since precipitated aluminum phosphate is soluble in a solution of sodium hydroxide, this solvent was tried in varying strengths, *viz.*, one, five, and ten per cent. Three portions of wavellite (0.2 gram each) were treated with 100 cc. of the different strengths of solvent in an Erlenmeyer flask carrying a condenser. The flask was kept in a boiling water bath for five hours. The solution was filtered and the phosphoric anhydride determined in the usual manner. One per cent. solution extracted 99.4 per cent. of the phosphoric anhydride in the mineral; five per cent. solution extracted 94.3 per cent., as did the ten per cent. solution. Accordingly, one per cent. solution of sodium hydroxide was chosen for the experiments. Sodium hydroxide free from phosphates was used. To try the effect of the one per cent. caustic soda on the other minerals, 0.2 gram each of dufrenite and apatite were treated with 100 cc. of the one per cent. sodium hydroxide solution. Dufrenite yielded 90.4 per cent. of its phosphoric anhydride to this solvent, and apatite 8.4 per cent.

Fraps[1] gives the result of the action of various acid solvents on several kinds of phosphates, mineral and precipitated. From his table it is to be noted that fifth-normal nitric acid acting at a temperature of 40° for five hours extracts 100 per cent. of phosphoric anhydride in apatite, 1.5 per cent. in dufrenite, and 3.6 per cent. in wavellite.

The minerals used by the writer, taking as before 0.2 gram of mineral and 100 cc. of solvent at 40°, gave for apatite 95.4 per cent. of phosphoric anhydride extracted, for the dufrenite 4.4 per cent., and for the wavellite 9.4 per cent. Using this same strength of acid in a boiling water bath for five hours, 100 per cent. of the phosphoric anhydride in the apatite was extracted, 58.9 per cent. in the wavellite, and 8.2 per cent. in the dufrenite. From these results it can be seen that it is necessary to keep the temperature at 40° during the five hours of extraction.

In using these solvents on the soil it was assumed that there would be extracted, in the case of sodium hydroxide solution, the iron and aluminum phosphates, but not the calcium phosphate, and in the case of the fifth-normal nitric acid, the calcium phosphate but not the iron and aluminum phosphates; or at least that there would be extracted proportional parts of the phosphates wherever there might be inclusion of the minerals within the soil grains. In every case, samples which had been passed through a 100-mesh sieve were used.

Twelve soils were selected, six of them not acid and six of them acid, as shown by the usual litmus paper test. The history of the various soils follows:

No. 523, from Mayville.—Cropped sixty years to grains; during the later years a four-year rotation has been practiced with clover and timothy, and manure has been applied. Yields good, and fertility is maintained. Not acid.

No. 270, from Blue Mounds.—Cropped sixty years to grains. Clover now raised and manure applied so that the yields are good and fertility is maintained. Not acid.

No. 865, from Evansville.—Cropped fifty-seven years to grains and considerable tobacco. Manured heavily for tobacco, and crops are good. Not acid.

No. 127, from Superior.—Raised but few crops of wild hay. Fertilizer tests in the plant house showed a slight lack of available phosphates. Not acid.

No. 61, from Stanley.—Cropped about ten years; very poor yields, differing from rest of this region. Plant house test showed need of phosphates. Not acid.

No. 618, Plot 6, Station Farm at Madison. Cropped about 25 years in rotation to corn, oats, seeded to clover, clover and potatoes, and manured on clover sod. Not acid.

No. 293, from Twin Bluffs.—Cropped forty years; some wheat, corn, and oats; crops sold off; the soil has been kept up for twenty years. Field test showed need of phosphates. Acid.

No. 736, from Afton.—Cropped sixty-one years to grains, a little manure has been applied; oats poor; responded to phosphate in the field. Acid.

No. 852, from Evansville.—Cropped fifty years

[1] "Availability of Phosphoric Acid of the Soil," *J. Am. Chem. Soc.*, **28**, 824.

to grains, some tobacco; manured for tobacco. Has been badly exhausted; not quite so bad now. Responded to phosphate in the field. Acid.

No. 246, from Onalaska.—Cropped about forty years to corn and oats; little or no clover; badly exhausted. Field test showed need of phosphates. Acid.

No. 277, from South Wayne.—Cropped sixty years, first to wheat, then mixed farm crops with some stock kept on the place; crops all removed; is badly depleted. Field test showed need of phosphates. Acid.

No. 297, from Black Earth.—Cropped twenty years in rotation and fairly well managed; it is in fair state of fertility. Field tests showed need of phosphates. Acid.

It is to be noted that all of these soils have been cropped from ten to sixty years, except one which has been under cultivation but a few years. One soil, No. 127, is a heavy red clay; the others are loams with varying amounts of sand and clay.

Twenty-five grams of soil were treated with 250 cc. of solvent in a flask fitted with a ground glass stopper carrying a condenser. For the sodium hydroxide solvent the flask was set in a boiling water bath and shaken every hour. At the end of five hours it was allowed to cool, filtered through a dry filter, twice if necessary, to remove the clay. The sodium hydroxide extracted some of the humus in the soil, so that the liquid was black in color. It was necessary to remove this organic matter before determining the phosphoric anhydride extracted by sodium hydroxide from the minerals. Accordingly, duplicate portions of 100 cc. each were placed in test tubes, made slightly acid with 2 cc. of concentrated hydrochloric acid, placed in a centrifuge and whirled at a speed of about 1,200 revolutions per minute for 15 minutes. The slimy organic matter, or "humic acid," as it is popularly called, was firmly packed in the bottom of the test tube by this treatment, and the clear, supernatant liquid could be readily decanted through a dry filter. Aliquot portions of the filtrate were then oxidized with bromine to remove some organic matter which remained in solution. It is unfortunately not possible to throw all of the organic matter out of the solution by acid, but the amount left is very small, and the phosphoric anhydride in this organic matter would be practically nil, since, as we shall see later, the phosphoric acid, even in a true humic extract, is very small in amount. After the extraction of the organic matter the solution is acidified with nitric acid, and evaporated to dryness, silica dehydrated, then taken up with nitric acid and water and filtered. From this point the usual methods for determining phosphoric acid were employed. It may be well to state that, although the gravimetric method was used wherever possible, in many cases the amount of phosphoric acid was so small that this method was not feasible. In such cases the yellow precipitate was dissolved in standard caustic soda and the excess titrated with standard nitric acid. While it is well to note that the volumetric method is apt to give high results, it has been found that working with very small amounts the method is reasonably accurate, certainly much more so than the gravimetric method where it would be necessary to weigh a precipitate of considerably less than one milligram in weight.

Where the soils were treated with fifth-normal nitric acid the temperature of the water bath was kept at 40° for five hours, the flasks being shaken every hour. After filtering off the soil the clear filtrate was found to contain a very small amount of organic matter dissolved by the nitric acid. The solution, accordingly, was made slightly alkaline with sodium hydroxide, oxidized with bromine, acidified with nitric acid, evaporated to dryness, silica dehydrated, etc., as before.

In addition to the above-mentioned determinations, it was thought advisable to make a brief study of the phosphoric acid combined with the humus. It is well known that the humus of the soil—that black, waxy coating of the soil grains—contains in chemical combination some phosphoric acid, as well as other inorganic compounds. The question had arisen as to the composition and amount of humus in well-drained, cropped, acid soils as compared with non-acid soils. The only method available for this work was the usual extraction with ammonia after treatment with hydrochloric acid, but in this method there are certain weak points to be avoided. The determination of humus by loss on ignition of the dried extract is open to two objections: First, the heating causes loss of zeolitic water from the clay which remains in suspension in the solution and cannot be removed by ordinary filtering; and, second, even if the clay were removed, the result would represent only the volatile compounds in the humus and not the important ash constituents which are certainly a part of the humus.

It has been possible to remove the clay by filtering through an unglazed porcelain filter, but this removes some of the organic matter with the clay, since the humus extract is not in all respects a true solution but has some properties of a colloid.

After the clay is removed the humus must be precipitated by an acid, since the ammonia extracts some of the phosphoric acid from the minerals in the soil. Fraps[1] shows that samples of apatite, dufrenite, and wavellite extracted by ammonia yielded 3 per cent., 13 per cent., and 44 per cent. of phosphoric anhydride, respectively. He used material corresponding to 0.1 gram phosphoric anhydride, shaken with 2,000 cc. of 4 per cent. ammonia at intervals for 24 hours and then filtered. The minerals used by the writer, when treated in 0.2-gram portions with 500 cc. of 4 per cent. ammonia for 24 hours with shaking and then 12 hours at rest, yielded approximately 1 per cent. for apatite, 3 per cent. for dufrenite, and 55 per cent. for wavellite. These results show that it is unsafe to determine the phosphoric acid in the ammoniacal extract and call it all humic phosphate.

Fraps, in the article just referred to, makes use of ammonium sulphate to flocculate the clay in the ammoniacal extract of the soil, and this method was pursued in the following experiments. Hydrochloric acid was used to precipitate the humus, since this acid has been found[2] to give better results than nitric acid; the filtrate is less colored by soluble organic matter. The humus is not completely precipitated even by hydrochloric acid, but is practically so.

The method as used in this work was to treat 25 grams of soil in a glass stoppered bottle with 400 cc. of 1 per cent. hydrochloric acid for 1 hour, shaking constantly in a mechanical shaker. Then it was filtered through a Büchner funnel on which had been placed a hardened filter paper. The soil was washed free from chlorides and transferred to a liter Erlenmeyer flask with 500 cc. of 4 per cent. ammonia and shaken at intervals for 24 hours. At this point 25 cc. of ammonium sulphate solution, containing 10 grams of the solid, were added, the mixture shaken and allowed to stand over night. When filtered through ordinary filter paper the filtrate was absolutely free from clay, the latter containing little, if any, gelatinous organic matter, and the filtration proceeded rapidly. For the determination of humus, 50 cc. were placed in a heavy test tube, acidified with 8 cc. concentrated hydrochloric acid and whirled in the centrifuge. The supernatant liquid was decanted through a weighed Gooch crucible, the humus transferred to the Gooch, washed with 1 per cent. hydrochloric acid, dried at 105° and weighed.

The humic phosphate was determined on an aliquot portion of the extract, treated in test tubes with hydrochloric acid, whirled in the centrifuge, filtered, and washed. The precipitate was dissolved through the paper with 1 per cent. sodium hydroxide solution, the paper washed clean with sodium hydroxide solution, and the organic matter oxidized with bromine, then acidified with nitric acid, evaporated dry, the silica dehydrated, and the phosphoric anhydride determined volumetrically, since the amount of yellow precipitate was very small.

Some preliminary trials of this method where the filtrate from the humus, as well as the humus, was analyzed for phosphoric anhydride, showed that there was about four times as much phosphoric anhydride in the filtrate as in the precipitate. This represents for the most part the phosphoric anhydride extracted by ammonia from the minerals of the soil.

Table I gives the percentages of the total phosphoric anhydride, phosphoric anhydride extracted by 1 per cent. sodium hydroxide solution, phosphoric anhydride extracted by fifth-normal nitric acid, phosphoric anhydride in the humus, and the humus, all expressed on the basis of dry soil; then the average percentages of phosphoric anhydride extracted by sodium hydroxide, by nitric acid, and in humus expressed on the basis of total phosphoric anhydride, and finally the humic phosphoric anhydride expressed on the basis of humus, besides the arithmetical averages of the different results.

The figures given in the averages show that, while acid soils do not contain more iron and aluminum phosphates than do non-acid soils, they do contain a larger percentage of their total phosphoric acid in the iron and aluminum form, and in addition a considerably greater ratio of iron and aluminum phosphates to calcium phosphate—three to one for acid soils, and about one and one-half to one for non-acid soils.

Turning now to the phosphoric acid soluble in

[1] "The Ammonia-soluble Phosphoric Acid of the Soil." *Am Chem. J.*, **39**, 580.

[2] Unpublished results of H. L. Walster, Soils Dept., Univ. of Wis.

fifth-normal nitric acid, it is seen that considerably more is extracted from the non-acid soils than from the acid soils. In other words, the non-acid soils contain more calcium phosphate than do the acid soils. This is to be expected if soil acidity is the cause of the lack of available phosphates.

But, aside from this consideration, the figures show another interesting fact. It will be remembered that two of the non-acid soils responded to a phosphate fertilizer, Nos. 61 and 127. All of the acid soils have shown the lack of available phosphates. The average per cent. of phosphoric acid soluble in nitric acid of the four soils which do not need phosphate, is 0.036 per cent., and of the eight soils which do need phosphate is 0.012 per cent.—three times as much calcium phosphate in non-responsive soils as in responsive soils.

nutrition of the crop depends on the rate at which the fertilizing elements become available, and not upon the total amount present at any one time; but from these figures, it appears that the amount of calcium phosphate in a soil gives a very excellent idea as to the requirements of a soil with reference to phosphoric acid. In other words, there is a strong probability that the value of the fifth-normal nitric acid as an indicator of soil needs lies in the fact that it determines the amount of calcium phosphate in the soil, and does not merely imitate the solvent action of plant roots. From the results obtained in this work, it can be stated that, for Wisconsin at least, if a soil contains less than 0.015 per cent. of phosphoric acid soluble in fifth-normal nitric acid, it will respond to a phosphate fertilizer.[1]

Considering Table I again, it is to be noted that the humus content of the two sets of soils

TABLE I

PERCENTAGES OF PHOSPHORIC ACID AND HUMUS.

No. of sample.	Total P_2O_5.	P_2O_5 by NaOH	Per cent. of total.	P_2O_5 by HNO_3	Per cent. of total	Humic P_2O_5	Per cent of total	Humus	Humic P_2O_5 per cent of humus	Years cropped	Locality
SOILS NOT ACID.											
523	0.14	0.039	27.86	0.025	17.86	0.013	9.28	0.72	1.81	60	Mayville
270	0.18	0.054	30.00	0.023	12.78	0.007	3.89	1.10	0.64	60	Blue Mounds
865	0.08	0.046	57.50	0.035	43.75	0.011	13.75	0.51	2.16	57	Evansville
127	0.15	0.039	26.00	0.010	6.67	0.009	6.00	0.19	4.74	3	Superior
61	0.19	0.080	42.10	0.010	5.26	0.022	11.58	0.69	3.19	10	Stanley
618	0.18	0.030	16.67	0.063	35.00	0.014	7.78	0.63	2.22	25	Madison
Average.....	0.153	0.048	33.35	0.027	20.22	0.012	8.71	0.64	2.46	35	
SOILS ACID											
293	0.12	0.038	31.67	0.012	10.00	0.007	5.83	0.28	2.50	40	Twin Bluffs
736	0.07	0.053	75.21	0.027	38.57	0.008	11.43	0.67	1.19	61	Afton
852	0.13	0.073	56.15	0.009	6.92	0.011	8.46	1.19	0.92	50	Evansville
246	0.12	0.014	11.67	0.011	9.17	0.011	9.17	0.30	3.67	40	Onalaska
277	0.14	0.018	12.86	0.007	5.00	0.009	6.43	0.17	5.29	60	South Wayne
297	0.17	0.054	31.76	0.014	8.24	0.019	11.18	1.51	1.25	20	Black Earth
Average..........	0.125	0.041	36.63	0.013	12.98	0.011	8.74	0.68	2.47	45	

TABLE II.

HUMUS AND PHOSPHORIC ACID IN HUMUS.

Humus....................	1.51	1.19	1.10	0.72	0.69	0.67	0.63	0.51	0.30	0.28	0.19	0.17
P_2O_5 in humus............	1.25	0.92	0.64	1.81	3.19	1.19	2.22	2.16	3.67	2.50	4.74	5.29

Dilute nitric acid has been used by investigators with more or less success as an indicator of soil needs and the results here given show the value of fifth-normal nitric acid in determining the availability of phosphates in the soil. It seems reasonable to suppose that this is because the nitric acid dissolves out but little more than the calcium phosphate, and if calcium phosphate exists in too small amount the plant suffers for lack of phosphorus. Ordinarily a chemical analysis of the soil is of very little value in ascertaining the fertilizer requirements of a soil, inasmuch as the

is about the same, and the phosphoric anhydride in the humus is also about the same in both acid and non-acid soils, indicating that the reaction of the soil does not affect the accumulation of phosphoric acid in the humus. If, however, the soils are arranged in the order of their humus content from highest to lowest, together with the corresponding percentages of phosphoric an-

[1] In this connection it is interesting to note the following statement by Harry Snyder in *Minn. Bull.*, **102,** p. 36: "In all the trials, with the one exception noted, where the phosphate fertilizer failed to give an increase, the soil contained over 150 parts per million of phosphoric acid soluble in fifth-normal nitric acid." The two similar conclusions were drawn independently, and from work done on different soils.

hydride expressed on the basis of humus, it will be seen in a general way that as the amount of humus decreases the percentage of phosphoric anhydride in the humus increases (see Table II). Arranging the soils in groups of three, and averaging the percentages just expressed, this fact is brought out more strikingly (Table III). These results suggest the possibility that phosphorus in humus is not made available to plants as the humus decomposes, but rather that the phosphorus once in the humic form is unavailable to plants. This point is to be tested on comparable virgin and cropped samples of soils, and in addition further work is contemplated on the changes taking place in a soil during its period of cropping. Acid and non-acid soils will be used, these same soils so far as possible, but the study will be made on the differences that exist in the phosphate compounds between the virgin and the cropped samples.

TABLE III.

HUMUS AND PHOSPHORIC ACID IN HUMUS. AVERAGED IN GROUPS OF THREE.

Humus	1.27	0.69	0.48	0.21
P_2O_5 in humus	0.93	2.06	2.68	4.17

Summarizing the results, it is to be observed:

First, that acid soils lack available phosphates.

Second, that soil acidity seems to cause a lack of available phosphates, since acid soils contain a higher percentage of their total phosphoric acid in iron and aluminum form and less calcium phosphate than do non-acid soils, and particularly a greater ratio of iron and aluminum phosphates to calcium phosphate. This does not mean that non-acid soils may not be lacking in available phosphates, due to some other cause.

Third, that the figures on humus and phosphoric anhydride in humus show an interesting variation, suggesting that humic phosphorus may be unavailable to plants.

Fourth, that fifth-normal nitric acid is an excellent indicator of soil needs with respect to phosphates, due to the fact that it determines the amount of calcium phosphate in soils. If a soil, in Wisconsin at least, falls below 0.015 per cent. of phosphoric acid soluble in fifth-normal nitric acid, it will respond to phosphate fertilizer.

DEPARTMENT OF SOILS,
AGRICULTURAL EXPERIMENT STATION,
UNIVERSITY OF WISCONSIN.

A REMARKABLE ACCUMULATION OF NITROGEN, CARBON AND HUMUS IN A PRAIRIE SOIL.

BY F. J. ALWAY AND C. E. VAIL.

Received November 14, 1908.

Lawes and Gilbert[1] in 1885 reported the analysis of a sample of soil from Selkirk, Manitoba, showing 0.618 per cent. of nitrogen in the first foot. This has since been commonly used by writers as an illustration of the extent to which nitrogen may accumulate in virgin prairie soils. "The soil from Selkirk was taken from a farm which had been in cultivation for 25 years, but from a portion near the buildings which had never been broken up." Lawes and Gilbert, neither of whom had seen the farm, recognized the remarkable composition of the sample but evidently considered it representative of the soil area. The explanation of the composition of the sample may, however, be the same as that of the still higher percentages in the case of some samples taken by the senior author of this article from near Indian Head, Saskatchewan, in October, 1907.

Selkirk is situated in the bed of glacial Lake Agassiz,[2] now the so-called Red River Valley, the soil being a lacustral clay. The contemporaneous glacial Lake Saskatchewan[3] covered a considerable area in what is now the province of Saskatchewan, which adjoins Manitoba on the west. The characteristic soil covering its bed is likewise a lacustral clay. The soils of these two areas, being formed from similar sources and at the same time as well as having since been subjected to more or less similar climatic conditions, may reasonably be expected to have many characteristics in common.

A considerable number of individual samples were taken from a tract of virgin prairie adjacent to the Indian Head experimental farm in order to be able to form some idea as to the differences in composition between the surface soils of the two types before they were brought under cultivation. All the samples were taken with a brass tube 1-3/8 inches in diameter, provided with a wide collar six inches from the end. The tube was driven into the ground until the collar rested firmly on the surface of the soil.

Two types of soil occur both in the prairie tract and on the experimental farm, *viz.*, boulder clay

[1] *Jour. Chem. Soc.*, **1885**, Proc., pp. 380-422.
[2] Upham, *Lake Agassiz*, *U. S. Geol. Survey*, **1895**.
[3] *Ibid.*

or till as well as lacustral clay. Both types have previously been described.[1] The most clayey parts of the latter, which also form the lowest lying portions, are characterized by small hummocks two or three feet in diameter and about six inches high. These hummocks are often not noticed until one drives over the prairie in a carriage. They are probably similar in origin to the "hog-wallows"[2] of the southwestern United States. Three individual samples were taken from the till, three from the summits of the hummocks and three from the rifts at the edges of the latter. Besides these nine samples, four were taken from modified rifts and divided into one-inch sections, in order to determine the vertical distribution of humus and nitrogen. The rifts from which these four cores were taken differed from those from which 720, 721 and 722 were secured in that they were rounded and entirely grassed over, as though considerable time had elapsed since they had been active rifts, *i. e.*, opening in time of drouth and closing when the soil was thoroughly moistened. These were selected for the inch sections on the supposition that they would be intermediate in humus and nitrogen between the active rifts and the summits of the hummocks, it not being suspected that there would be found the great differences between the two which the analyses have since revealed.

The humus was determined by Grandeau's method as modified by Hilgard. To determine the humus nitrogen the ammoniacal solution of humus was evaporated to a small volume, magnesium oxide added, the solution boiled again and the nitrogen in the residue finally determined by the usual Kjeldahl method. The organic carbon was determined by combustion with copper oxide.

There are no marked differences in composition between the till and the soil from the summits of the hummocks. The rifts, however, show an entirely different character, being more than twice as rich in humus, humus nitrogen, total nitrogen and carbon. The humus of the rifts is somewhat richer in nitrogen while the percentage of total nitrogen in the form of humus nitrogen is decidedly higher. The proportion of organic matter in the form of humus, as indicated by the last column, is practically the same in all samples. The percentage of nitrogen in the humus is about the same in all and, as elsewhere[1] pointed out, is similar to that in soils from humid regions.

RESULTS OF THE ANALYSES.

Soil No.		Humus Per cent	Humus ash. Per cent.	Humus nitrogen. Per cent	Total nitrogen. Per cent	Nitrogen in humus. Per cent.	Total nitrogen in form of humus nitrogen. Per cent	Ratio of humus to total nitrogen	Organic carbon. Per cent.	Ratio of organic carbon to total nitrogen.	Ratio of organic carbon to humus.
714	Boulder clay	2.73	1.04	0.153	0.341	5.6	44.8	8.0	3.94	11.6	1.4
715	" "	3.08	1.55	0.165	0.433	5.4	38.1	7.1	4.86	11.2	1.6
716	" "	2.71	1.13	0.137	0.374	5.1	36.6	7.2	4.22	11.4	1.6
Average	" "	2.84	1.24	0.152	0.383	5.4	39.8	7.4	4.34	11.4	1.5
717	Lacustral clay, summits of hummocks	3.25	0.86	0.176	0.440	5.4	40.0	7.4	4.64	10.5	1.4
718	" " " " "	2.77	0.68	0.160	0.363	5.8	44.1	7.6	3.93	10.8	1.4
719	" " " " "	2.53	0.64	0.130	0.352	5.1	36.9	7.2	3.65	10.4	1.4
Average	" " " " "	2.85	0.73	0.155	0.385	5.4	40.3	7.4	4.07	10.5	1.4
720	Lacustral clay, rifts between hummocks	7.16	1.23	0.488	0.836	6.8	58.4	8.6	11.13	13.3	1.6
721	" " " " "	7.60	1.56	0.479	0.867	6.3	55.2	8.8	10.54	12.2	1.4
722	" " " " "	6.77	1.13	0.414	0.809	6.1	51.2	8.4	10.11	12.5	1.5
Average	" " " " "	7.18	1.31	0.460	0.837	6.4	54.9	8.6	10.59	12.7	1.5
	Section of four cores from modified rifts.										
723	First inch	9.15	1.73	0.606	1.264	6.6	48.0	7.2	16.46	13.0	1.8
724	Second "	8.38	1.86	0.469	0.948	5.6	49.5	8.8	10.88	11.5	1.3
725	Third "	5.98	1.52	0.385	0.870	6.4	44.3	6.9	10.38	11.9	1.7
726	Fourth "	5.45	1.64	0.294	0.710	5.4	41.4	7.7	8.16	11.5	1.5
727	Fifth "	4.82	1.54	0.257	0.611	5.3	42.1	7.9	6.95	11.3	1.4
728	Sixth "	4.22	1.38	0.216	0.532	5.1	40.6	8.0	6.27	11.8	1.5
Average		6.33	1.61	0.371	0.822	5.7	44.3	7.7	9.85	11.8	1.5

[1] Alway, *Am. Chem. Jour.*, **31**, 580 (1906). Alway and McDole, *Ibid.*, **32**, 275 (1907). Alway, *Jour. Agr. Sci.*, **2**, 333 (1908).

[2] Hilgard, "Soils," p. 114.

[1] Alway and Trumbull, *Am. Chem. Jour.*, **40**, 147 (1908).

It is generally recognized that the extent to which a composite sample of soil is truly representative of a given area depends in a considerable degree upon the number of individual samples of which it is composed. In the case of virgin soils that are being investigated for the first time it is, however, important to make analyses of a number of individual samples as well as of composites. Had this not been done in the present instance, a composite made up of individual samples from the modified rifts would have been used as a representative of the lacustral clay. Another person in sampling the prairie might have omitted the rifts entirely. Both methods would have given very misleading results.

The analyses show that the soil of the modified rifts is very similar in composition to that of the active rifts. The probable explanation of the very high content of humus nitrogen and carbon is as follows: The wet season at Indian Head is usually of short duration, extending from about the middle of May to the middle of July.[1] During the dry weather the heavy clay cracks. The winds of late summer, autumn and spring fill the rifts with vegetable débris. With the return of the wet weather the clay expands, the rifts close, and the organic matter protected from eremacausis, undergoes partial humification. At the end of summer the dry weather causes the opening of the rifts, which then begin anew to collect plant débris.

It is apparent from the above data that it will be extremely difficult to estimate the original content of humus and of nitrogen in a field of lacustral clay that has long been under cultivation. The portion of the surface originally occupied by hummocks and rifts, which offer no serious obstacle to the plow, would need to be known, as well as the relation between the distribution of hummocks and the average composition of the soil.

During the past month four samples of prairie soil have been received from Mr. B. J. Reynolds, of Indian Head. They were six-inch samples taken with a wood auger, three being from rifts and one from an adjacent summit. The percentages of total nitrogen were, respectively, 0.85, 0.73, 0.65 and 0.26.

The similarity of the Selkirk soil described by Lawes and Gilbert to the rift soil from Indian Head is shown in the following:

[1] *Bull.* **130**, *Bureau of Plant Industry*, p 22 (1908).

	Total N.	Carbon	Ratio of carbon to nitrogen.
Selkirk soil (Lawes and Gilbert)	0.618	7.58	12.3
Indian Head soil from rifts	0.837	10.59	12.7
Indian Head soil from modified rifts	0.822	9.85	11.8

Laboratory of Agricultural Chemistry,
University of Nebraska,
Lincoln, Nebr.

RAPID DETERMINATION OF OIL IN COTTONSEED PRODUCTS.

By Chas. H. Herty, F. B. Stem and M. Orr.

Received November 10, 1908.

In the manufacture of cottonseed oil the delinted seeds are cut and the meats or kernels separated mechanically from the hulls. The meats are then mashed between heavy rollers, cooked in steam-jacketed vessels, and the oil expressed by hydraulic pressure. The determination of oil in the hulls gives a measure of the completeness of the separation of the meats from the hulls, while the oil content of the meal affords a control of the character of the press work. It would seem, therefore, that a prompt and constant knowledge of the oil content of the hulls and meal would be indispensable in the operation of a mill. However desirable, this is by no means the case in actual practice. Two explanations suggest themselves: first, the organization of the industry; second, the method of analysis employed. The erection of many small mills is made necessary by the bulky character of the cottonseed, with its consequent cost of transportation, and by the impossibility of storing large quantities of seed for any great length of time without marked deterioration. The output of many of these small mills is not sufficient to justify the employment of a trained chemist, and the time required for obtaining an analysis from a distant laboratory largely discounts the value of the knowledge gained, except in extreme cases. But even if a laboratory is close at hand, or in the mill itself, five or six hours must elapse before the result of the analysis reaches the mill from the laboratory, this on account of the method of analysis employed. A more general resort to chemical control could be expected, therefore, if a simple, and rapid method of analysis were available. The present investigation has been undertaken in the hope of filling this need. Furthermore, the purchase of cottonseed by the mills is conducted regardless of the oil content of the seed. It is hoped that the rapid method

here described may be of some service in this important matter.

OBJECTIONS TO PRESENT METHOD.

The method of analysis usually employed consists in extracting the oil from a sample in a Soxhlet extractor with redistilled, low-boiling petroleum ether, evaporating the extractive and weighing the residual oil.

The objections to the method are:

First, the extraction must be conducted at a relatively low temperature, this being determined by the temperature of the condensed extractive dropping upon the sample from the condenser above.

Second, in the Soxhlet apparatus it is necessary not only to completely extract the oil but to transfer it completely to the flask below by repeated siphonings.

Third, considerable time is consumed in the complete evaporation of the extractive.

Fourth, the limitation to a comparatively small sample of the substance.

Fifth, the danger of fire.

Sixth, the necessity of using rather expensive apparatus and the need of a supply of running water for the condensers.

Seventh, the necessity of employing a trained chemist to conduct the operations.

PROPOSED METHOD.

It is believed that all of these objections are met in the method here proposed. It consists in digesting a definite and relatively large quantity of the substance with a definite volume of carbon tetrachloride in a loosely stoppered Erlenmeyer flask for 15 minutes at a temperature of approximately 60° C., cooling to room temperature, shaking thoroughly, filtering, and determining the specific gravity and temperature of the filtered extract. From these observations the per cent. of oil is calculated. Detailed directions for the analysis of the several products follow:

Meal.—Forty grams of the thoroughly mixed sample of meal are transferred to a 250 cc. Erlenmeyer flask, which is then placed in a water bath previously heated to approximately 60° C. After heating the flask about 2 minutes 100 cc. of carbon tetrachloride are poured gently upon the meal through a funnel reaching almost to the surface of the meal. The flask is lowered in the water until the surface of the carbon tetrachloride is lower than that of the water, a cork loosely inserted and the extraction allowed to proceed. Slight variations in the temperature of the water bath do not affect the accuracy of the determination. The minimum time for the extraction is 15 minutes, it may be longer. When the extraction is completed the flask is cooled to room temperature, thoroughly shaken and the contents strained through wire gauze on to a folded filter, the gauze being squeezed to insure sufficient filtrate. The clear extract is caught in a specific gravity tube (5 inches by 1 inch test-tube on foot). This is filled to within 1 inch of the top, then tightly corked and placed in a vessel containing water at room temperature. After standing at least 10 minutes the tube containing the extract is placed in a 500 cc. plain beaker containing sufficient clear water, at room temperature, to reach the level of the extract in the tube. By this means too rapid change in the temperature of the extract is avoided. The cork is then removed, the specific gravity of the extract determined by the Westphal balance, and the temperature accurately noted from the thermometer placed within the plummet of the balance. Add or subtract the constant for the carbon tetrachloride in use and subtract the corrected specific gravity of the extract from that of the carbon tetrachloride shown in Table 6 at the same temperature. This difference is divided by 0.00286. The result is the per cent. of oil.

Hulls.—After removing whole seed from the sample of hulls, 40 grams are placed in an Erlenmeyer flask and slightly packed with a glass rod. This is necessary to insure complete covering of the bulky hulls by the extractive. 100 cc. of carbon tetrachloride are added. The rest of the determination is identical with that for meal, except that the gauze strainer is not necessary in filtering.

Meats.—The method is the same as for meal except that 10 grams of meats are used with 100 cc. of carbon tetrachloride. The per cent. of oil found is multiplied by four.

Seed.—The sample of seed is thoroughly pounded in an iron mortar and the mass passed through a meat chopper. Forty grams are used with 200 cc. of carbon tetrachloride. The method is the same as for meal except that the per cent. of oil found is multiplied by two.

Experimental.

THE EXTRACTION.

The well-known solvent power of carbon tetrachloride for fats, its relatively high boiling point,

its low heat of vaporization and its non-combustibility, naturally suggested this substance as a substitute for gasoline and ether as the extractive. A. P. Bryant,[1] using a Knorr extractor, demonstrated the rapidity of extraction of fats in foods and feedstuffs by carbon tetrachloride. But he proposed merely the substitution of carbon tetrachloride for ether or carbon bisulphide in the usual method of extraction and evaporation of the extractive.

In the following experiments the determinations were carried out as follows: five grams of a substance whose oil content had been determined by the Soxhlet method were transferred to a 500 cc. Erlenmeyer flask, 50 cc. of gasoline or carbon tetrachloride added, and the extraction allowed to proceed at room temperature and without shaking, in order to avoid the sticking of the solid particles to the walls of the flask above the extractive. After standing a definite time the flask was thoroughly shaken in order to insure uniformity of the extract. This was then filtered through a dry filter paper. The amount of dissolved oil was determined in 25 cc. of the filtrate by distilling off the extract in a hot air bath, the temperature being quickly raised to 140° C. during the last stages of the evaporation. The last traces of the extractive were removed from the distillation flask by blowing quickly into it through a glass tube inserted almost to the oily layer. From the weight of the oil the per cent. was calculated by multiplying by one hundred and dividing the product by two and a half.

Cottonseed Meal.—7.29 per cent. oil by Soxhlet extraction with gasoline.

TABLE 1.

Time of extraction.	Per cent. oil with gasoline.	Per cent. oil with carbon tetrachloride.
7½ minutes	6.72	2.84
15 "	7.32	7.10
30 "	7.34	7.22
60 "	7.28	7.30
120 "	7.32	7.46

To determine the influence of temperature upon the rate of extraction by carbon tetrachloride, a series of experiments was carried out as above except that the Erlenmeyer flasks were placed in a water bath heated to 50° C. The results follow:

TABLE 2.

Time.	Per cent. of oil.
3¾ minutes	7.08
7½ "	7.44
15 "	7.38

The marked increase in the extraction at 50° in 7½ minutes as compared with that at room temperature for the same time led to the hope that the time for complete extraction could be still further diminished by carrying out the determination near the boiling point of carbon tetrachloride. This hope was fully justified, for by making an extraction at 70° for 3¾ minutes, the percentage of oil was found to be 7.30.

Cottonseed Meats.—30.27 per cent. oil by Soxhlet extraction.

TABLE 3.

Time.	Temperature.	Per cent. of oil.
30 minutes	25°	29.22
30 "	35°	29.50
30 "	50°	30.38
30 "	70°	30.62

From these determinations it is evident that the time-consuming extraction with the Soxhlet apparatus is unnecessary and that an accurate determination of the oil in these products can be made with simple apparatus, in a much shorter time, and with no danger from fire.

RAPID DETERMINATION OF OIL IN EXTRACT.

In order to simplify and hasten the determination of oil in the extract experiments were begun on the lowering of the specific gravity of the carbon tetrachloride by the dissolved oil. The great difference in the specific gravity of carbon tetrachloride (1.62) and of cottonseed oil (0.92) gave a reasonable hope for success. In order to avoid possible difference in the specific gravity of the crude oil obtained from the presses and that left in the meal the experiments were carried out on samples of meal whose oil content was determined in the usual manner by the Soxhlet extractor. The simplicity of the Westphal balance suggested this method of determining the specific gravity. Comparison of the thermometer on the plummet of the balance used in the investigation with a standard thermometer showed it to be accurate between 15° and 30°.

A preliminary test, using 5 grams of meal and 50 cc. of carbon tetrachloride, as in the above experiments on the rate of extraction, showed that the method would probably be accurate to 1 per cent. The first step, therefore, was to determine the minimum time and temperature for extractions of larger proportions of meal, the volume of carbon tetrachloride being kept constant. A sample of cottonseed meal was passed through a 20-mesh sieve, and thoroughly mixed. In two portions of 10 grams each the oil was determined by the Soxhlet method, using redistilled gasoline

[1] *J. Am. Chem Soc.*, **26**, 568.

as the extractive in one case and chemically pure carbon tetrachloride in the other. With the former the percentage was found to be 8.68; with the latter 8.67.

With this meal extractions were made according to the method outlined above. In each case allowance was made for the constantly increasing volume of oil in the extract. The results follow:

TABLE 4.

No.	Grams of meal.	cc. of carbon tetrachloride.	Time (minutes).	Temperature	Per cent. of oil. I.	II.
1	10	50	5	70°	8.67	....
2	15	50	5	70°	8.58	....
3	20	50	5	70°	8.60	8.63
4	25	50	5	70°	8.18	....
5	30	50	5	70°	8.56	....

From the per cent. found in No. 5 it is evident that the low result in No. 4 was due to analytical error.

The use of 30 or even 25 grams of meal was found to be impracticable, as it was found to be impossible to secure sufficient filtrate for use with the Westphal balance. But with 20 grams sufficient filtrate could be obtained by using a strainer of brass or iron gauze and squeezing the extract on to a crimped filter. In order to avoid possible error in the specific gravity determinations due to the small amount of filtrate the proportions were increased to 30 grams of meal and 75 cc. of carbon tetrachloride. For the specific gravity determination a test-tube-on-foot 5 inches long and 1 inch in diameter was used. A magnifying glass was used in reading the thermometer on the plummet of the balance.

TABLE 5.

SPECIFIC GRAVITY OF CARBON TETRACHLORIDE.

Temperature.	Specific gravity.
15°	1.6041
20°	1.5951
25°	1.5861
30°	1.5771

Since these figures show a regular variation of 0.0090 for each 5 degrees the figures for intermediate temperatures are interpolated as follows:

TABLE 6.

Temperature.	Sp. gr.	Temperature.	Sp. gr.	Temperature	Sp. gr.
15.0°	1.6041	17.2°	1.6001	19.4°	962
.2°	037	.4°	1.5998	.6°	958
.4°	034	.6°	994	.8°	1.5955
.6°	030	.8°	991	20.0°	1.5951
.8°	027	18.0°	987	.2°	947
16.0°	023	.2°	983	.4°	944
.2°	019	.4°	980	.6°	940
.4°	016	.6°	976	.8°	937
.6°	012	.8°	973	21.0°	933
.8°	009	19.0°	969	.2°	929
17.0°	005	.2°	965	.4°	926

TABLE 6—(*Continued*).

Temperature	Sp. gr.	Temperature.	Sp. gr.	Temperature.	Sp. gr.
21.6°	922	24.4°	872	27.2°	821
.8°	919	.6°	868	.4°	818
22.0°	915	.8°	1.5865	.6°	814
.2°	911	25.0°	1.5861	.8°	811
.4°	908	.2°	857	28.0°	807
.6°	904	.4°	854	.2°	803
.8°	901	.6°	850	.4°	800
23.0°	897	.8°	847	.6°	796
.2°	893	26.0°	843	.8°	793
.4°	890	.2°	839	29.0°	789
.6°	886	.4°	836	.2°	785
.8°	883	.6°	832	.4°	782
24.0°	879	.8°	829	.6°	778
.2°	875	27.0°	825	.8°	1.5775

Meal.—To determine the lowering of the specific gravity of the carbon tetrachloride by increasing quantities of extracted oil a meal of known oil content (8.82 per cent.) was used. Quantities of this meal were used representing 30-gram portions each of 5.0, 7.5, and 10.0 per cent. meals; thus for

5.0 per cent. used 17.0068 grams;
7.5 per cent. used 25.5102 grams;
10.0 per cent. used 34.0135 grams.

These portions were extracted, each with 75 cc. of carbon tetrachloride in Erlenmeyer flasks for 5 minutes at 70°. The filtered extracts showed the following specific gravities:

TABLE 7.

Temperatures.	5 per cent.	7.5 per cent	10 per cent.
15°	1.5900	1.5830	1.5758
20°	1.5810	1.5740	1.5668
25°	1.5720	1.5650	1.5578

The same difference in specific gravity of 0.0018 for each degree of temperature is observed here as was found with the carbon tetrachloride alone, but the decrease in specific gravity due to the increasing quantities of oil is not quite so regular. Thus the decrease due to the oil in 30 grams of a 5 per cent. meal is 0.0141, but in a 10 per cent. meal 0.0283. To test this more carefully a new and more delicate Westphal balance was obtainedl The meal used contained 8.20 per cent. of oi.. Quantities of this meal were used, representing 40 gram portions each of 5 and 10 per cent. meals, the volume of carbon tetrachloride being increased accordingly to 100 cc. In order to avoid too rapid change in the temperature of the extract during the determination of the specific gravity, the tube containing the extract was placed in a 600 cc. plain beaker filled with clear water to the level of the extract. Different specimens of carbon tetrachloride were used in the two sets of experiments. Corrections for temperature were made on the basis of 1° = 0.0018 difference in specific gravity.

TABLE 8

FIVE PER CENT. MEAL.

SPECIFIC GRAVITY OF CARBON TETRACHLORIDE AT 26.4° = 1.5866.

Extract.	Temperature.	Specific gravity	Calculated to 26.4°.	Difference.
No. 1	26.7°	1.5718	1.5723	0.0143
No. 2	26.8°	1.5716	1.5723	0.0143

TEN PER CENT. MEAL

SPECIFIC GRAVITY OF CARBON TETRACHLORIDE AT 24° = 1.5918

Extract.	Temperature.	Specific gravity.	Calculated to 24°.	Difference.
No. 1	24.0°	1.5632	1.5632	0.0286
No. 2	24.2°	1.5628	1.5632	0.0286

The decrease in specific gravity is, therefore, regular and each per cent. of oil lowers the specific gravity 0.00286 when 40 grams of meal and 100 cc. of carbon tetrachloride are used. The per cent. of oil in a meal is obtained, therefore, by determining at the same temperature the difference between the specific gravity of the carbon tetrachloride and the filtered extract from 40 grams of the meal digested with 100 cc. of the carbon tetrachloride, and dividing this difference by 0.00286.

CONSTANT FOR CARBON TETRACHLORIDE.

The difficulty in securing different lots of commercial carbon tetrachloride of exactly the same specific gravity led to experiments with a grade differing widely from that used in the earlier part of the investigation. The following results were obtained:

TABLE 9.

Temperature.	Sp. gr. original carbon tetrachloride.	Sp. gr. new carbon tetrachloride.	Difference.
15°	1.6041	1.5903	0.0138
20°	1.5951	1.5813	0.0138
25°	1.5861	1.5723	0.0138

Having determined this difference, 0.0138, in all operations with this new lot, corrections should be made by adding the constant to the observed specific gravity and immediate reference could be made to the table of specific gravity of the original carbon tetrachloride. Such a procedure would obviate the necessity of using a thermostat. To test this, 40 grams of meal containing 8.50 per cent. of oil were digested with 100 cc. of the new lot of carbon tetrachloride for 5 minutes at 70°. The extract showed a specific gravity of 1.5572 at 20°; adding the constant 0.0138 this becomes 1.5710, a difference of 0.0241 from the original carbon tetrachloride. Dividing by 0.00286 the per cent. was found to be 8.43.

TIME AND TEMPERATURE EXPERIMENTS.

Some specimens of commercial carbon tetrachloride boil at lower temperatures than that of pure carbon tetrachloride (76.7°). It was deemed advisable, therefore, to determine the rate and completeness of extraction at lower temperatures. In the determinations the per cents. were obtained by the specific gravity method, using a meal whose oil content had previously been found to be 8.82 per cent. The results follow:

TABLE 10.

Temperature.	5 min.	10 min.	15 min.	20 min.	30 min.	Standing over night.
25°	7.32	7.50	7.32	7.50	8.00	8.16 8.19
25°[1]	7.50	....	8.00 7.81	..	7.93	..
40°	7.72	7.72	7.88	..	..	..
50°	7.72	8.35	8.72	..	..	..
60°	8.06	8.06	8.75	..	..	..
	8.08	8.06	8.81	..	..	..

From this table it is evidently impracticable to work at room temperatures. The results show, however, that a complete extraction is obtained in 15 minutes at temperatures 50°–60° C. At such temperatures there is no risk of the commercial carbon tetrachloride boiling.

Confirmation of the accuracy of the method for cottonseed meal is furnished by the following check analyses, for many of which we are indebted to Mr. Jas. B. Pratt, chemist of the Southern Cotton Oil Co., Charlotte, N. C., and Mr. O. L. Spurlin, chemist of the Georgia Cotton Oil Co., Atlanta, Ga.

TABLE 11.

No.	Soxhlet extraction	Specific gravity method. I.	II.
1	8.81	8.72	..
2	6.47	6.44	..
3	6.49	6.59	6.56
4	7.17	7.25	7.27
5	6.47	6.47	..
6	7.17	7.22	7.28
7	7.13	7.19	7.11
8	6.69	6.78	6.69
9	6.27	6.31	6.22
10	6.47	6.56	..
11	7.17	7.06	..
12	6.27	6.35	6.34
13	7.13	7.06	..
14	6.69	6.59	..
15	7.20	7.17	7.23
16	6.70	6.71	..
17	5.96	5.94	..
18	6.40	6.43	..

Meats.—Since the per cent. of oil in meats is high and varies between approximately 28 and 36 per cent., it was decided to use 10 grams of meats, instead of 40 as in the case of meal, with 100 cc. of carbon tetrachloride, in order to bring the specific gravity within the limit already worked out for meal, multiplying the per cent.

[1] Shaking at intervals.

found by four for the actual per cent. of oil in the meats. The use of a wire gauze strainer was unnecessary with meats.

TABLE 12.

PER CENT OF OIL IN UNCOOKED MEATS.

Temperature.	Time.	I.	II.
70°	5	27.12	27.40
70°	15	29.12	29.28
70°	30	29.44	...
60°	15	29.28	...

From these results it is evident that the standard time and temperature of extraction of meal is suited also for extraction of the one-fourth quantity of meats. Experiments using a larger proportion of meats showed low results. Whether this was due to incomplete extraction or to a possible change of the specific gravity curve for such high per cents. was not determined.

TABLE 13.

PER CENT. OF OIL IN COOKED MEATS.

Temperature.	5 min.		10 min		15 min.	
	I.	II.	I.	II.	I.	II.
50°	29.84	...	29.72	...	29.60	29.72
60°	29.60	...	29.88	...	30.34	...
70°	29.40	29.88	30.22	30.76	...	...

Again the extraction at 60° for 15 minutes is sufficient.

That the presence of moisture does not affect the extraction was demonstrated by extractions on both raw and cooked meats, at 60° C., for 15 minutes, thus:

TABLE 14.

	I.	II.
RAW MEATS (moisture 8.95):		
Hydrous	29.28	...
Anhydrous	29.40	29.12
COOKED MEATS (moisture 5.73):		
Hydrous	30.84	...
Anhydrous	31.40	31.00

Hulls.—After transferring 40 grams of hulls to the Erlenmeyer flask it was found necessary to pack the hulls with a glass rod in order to insure complete covering with 100 cc. of carbon tetrachloride. No wire gauze strainer was necessary in filtering the extract.

TABLE 15.

	Time.	Per cent. of oil.	
Temperature.	Min.	Soxhlet extraction.	Sp. gr. method.
60°	5	0.30	0.25
60°	10	..	0 32
60°	15	..	0.25
60°	30	..	0.25

It is proposed to extend the investigation to the determination of oil in linseed products, and of fats in feedstuffs, tankage, etc.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C., OCTOBER 29, 1908.

DETERMINATION OF SULPHUROUS ACID OR SULPHITES OR SULPHUR DIOXIDE IN FOOD PRODUCTS.[1]

BY EDWARD GUDEMAN.

Received October 27, 1908.

The method for the determination of sulphurous acid or sulphites or sulphur dioxide in food products as given in the Official and Provisional Methods of Analysis, Bulletin **107**, revised, Bureau of Chemistry, Dept. of Agriculture, having been accepted by the Association, is the standard or official method of analysis.

The essential part of the method calls for a direct distillation of 100 grams of the food product (with or without addition of water) acidified with 5 cc. of 20 per cent. glacial phosphoric acid, distilling into an excess of a standard iodine solution and titrating back the excess of iodine; the distillation is considered complete when 50 cc. have distilled over. In the analysis of meats and meat products the phosphoric acid is increased to 20 cc. (page 113), and in the examination of wines, direct titration of the sulphurous acid, without distillation, is permissible (page 188).

A large number of analyses of natural and prepared food products have shown that often weighable amounts of sulphur dioxide (or its compounds) will be obtained from food products that actually contain none at all, and when sulphur dioxide is present, the amount obtained by the official method will be in excess of the amount actually present, using the official method without modification. Many animal and vegetable food products normally contain sulphur compounds, which on distillation with acids give off volatile sulphur compounds, which react with the iodine solution and reducing the excess of standard iodine solution used, are thereby calculated to and considered and reported as sulphur dioxide present in the food product examined. Recognition of this source of error is taken when applying the method to the examination of meat and meat products, it being stated "mere traces should be ignored" (page 113). A like statement should be added to the official method itself, applying in the examination of all food products, ignoring the presence of "mere traces" of sulphur dioxide.

Sulphuretted hydrogen often liberated by the action of the acid, will react on the iodine solution and be reported to that extent as sulphur dioxide,

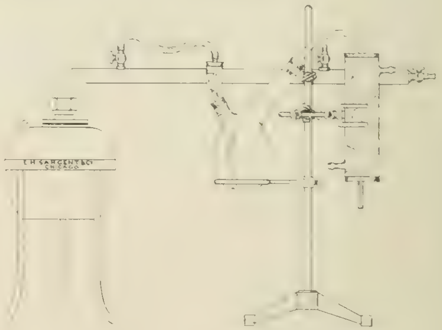
[1] Read before the Association of Official Agricultural Chemists, Nov., 1908.

unless the sulphides are separated by first passing the distillate through some solution of a metallic salt, as recommended by W. D. Horne and A. L. Winton. In many cases the sulphides can be held back by adding some metallic salt (cadmium, copper, silver, lead, etc.) directly to the product before beginning the distillation, thereby simplifying the process and not requiring the additional apparatus. Volatile sulphur compounds which do not appear as sulphuretted hydrogen and are not held back by the metallic salts, will react on the iodine solution and be calculated to and reported as sulphur dioxide present in the food product, and such volatile sulphur compounds will erroneously increase the amount of sulphur dioxide, free or combined, actually contained in the product.[1]

In the direct distillation of an acidified food product a high temperature of distillation is caused by the food product itself. During the direct distillation, concentration of the mass takes place and the acidity increases in nearly direct proportion to this concentration. With food products to which no water need be added for distillation, the original acidity (due to the added phosphoric acid) is 1 to 4 per cent. based on the product used (100 grams), and after distillation taking off 50 cc., the acidity will be nearly double 2 to 8 per cent., decomposition of the product increasing with the increasing acidity, giving rise to the peculiar volatile sulphur compounds. The decomposition of the food product due to the concentration, with increased acidity and high temperature, is often intensified by the previous treatment such prepared food product undergoes during its method of preparation, the "processing" of the product, especially noticeable with canned goods, which have been cooked or sterilized at high temperature. The analytical figures show that some fresh products, containing only traces or no sulphur dioxide in the raw state, after processing give strong reaction for sulphur compounds (see table). It was often found that a distillate of 50 cc. from a 100-gram sample was not sufficient to carry over all the sulphur dioxide and the other volatile sulphur compounds. Accidentally correct results may be obtained for sulphur dioxide, the distilled volatile sulphur compounds counterbalancing the loss of sulphur dioxide due to incomplete distillation, especially with such products that on heating become thick and gelatinous, causing foaming and bumping. Increasing the amount of the distillate produces greater decomposition, especially noticeable with food products, to which no water need be added for distillation, such as fruit juices, cordials, extracts, wine, beer, etc., all of which contain not over 20 per cent. non-volatile matter.

[1] Reports by W. D. Bigelow, F. Zerban and W. P. Naquin, *Proceedings A. O. A. C., Bull.* **116**, Bureau of Chemistry, issued Oct. 27, 1908.

The following simple modification of the official method has been found to eliminate many of these sources of error and to overcome most of the other objections raised. Instead of a direct distillation, the volatile products are driven over with low pressure steam. The steam is generated from distilled water and directly led into the mass. A good Bunsen burner will generate enough steam to make from 6 to 8 distillations at one time, within one hour, giving 4 to 500 cc. of distillate per sample. Any of the well-known water stills can be used, replacing the condensing coil with a copper tube, having sufficient stop-cock openings from which the steam is led through rubber tubing, into the retorts or distilling flasks containing the products to be analyzed. The accompanying sketch is self-explanatory.[1]



On account of condensation of steam during distillation, no possible concentration can take place, in fact dilution takes place and the retort or other distilling flask must be sufficiently large to accommodate this increase in bulk. Excessive condensation can be overcome by increasing the steam pressure or by using a small burner under the sand bath on which the distilling flask rests. The temperature of distillation can never increase above that of the steam used. Acidity cannot increase, in fact the acidity will decrease in nearly

[1] Continous water stills can be used if feed water is free from volatile sulphur compounds. Complete apparatus can be obtained from E. H. Sargent & Co., Chicago, to whom my thanks are due for the above illustration.

exact proportion as dilution takes place, due to the condensation on the sides of the retort. The steam entering below the surface of the mass acts as a mechanical stirrer and prevents foaming and bumping. Decomposition of the mass due to concentration, high temperature and increased acidity are eliminated and the distillate contains no volatile sulphur compounds due to such decomposition as found in the method with direct distillation. Using steam the amount of the distillate can be regulated and always can be sufficiently large (3–500 cc.) and of such character, that the sulphur dioxide can be determined by direct titration with iodine solution, as per method 2, page 168, Bull **107**, revised, thereby doing away with any error due to loss of iodine. For such direct titration of the distillate the method is modified by replacing the iodine in the absorption tube, beaker or flask, by a weak alkaline solution, a large beaker being most convenient. When distillation is complete, the starch indicator is added, distillate slightly acidified with hydrochloric, sulphuric or phosphoric acid and quickly titrated with a standard iodine solution.

The use of steam for distillation was found to have extended application, especially in the determination of sulphurous acid and its compounds and in the examination and determination of glycerin, ammonia, volatile fatty acids, alcoholic beverages, ether, aldehydes, extracts, turpentine, cereals, etc. and in obtaining distillates from substances that foam or bump.

Some comparative results in the determination of sulphur dioxide in food products are as follows:

SULPHUR DIOXIDE FOUND.
Parts per 100.

	Official method.		Modified method.	
Prepared samples.[1]	Direct titration.	After oxidation.	Direct titration.	After oxidation.
Sugar and added sulphites	0.0045	0.0045	0.0050	0.0050
Flour and added sulphites	0.0037	0.0040	0.0048	0.0048
Starch and added sulphites	0.0022	0.0022	0.0025	0.0025
Regular samples				
Gelatine (home-made)	0.0002	0.0006	0.0000	0.0000
Gelatine (French)	0.0270	0.0276	0.0260	0.0260
Gelatine (American)	0.0130	0.0142	0.0120	0.0121
Meat—fresh	0.0001	0.0004	0.0000	0.0000
Eggs—fresh	0.0003	0.0005	0.0000	0.0000
Eggs—age unknown	0.0003	0.0008	0.0000	0.0000
Dried fruit	0.0083	0.0087	0.0078	0.0077
Dried fruit	0.0240	0.0251	0.0228	0.0228
Molasses—bleached	0.0456	0.0476	0.0410	0.0414
Molasses—bleached	0.0300	0.0307	0.0288	0.0287
Molasses	0.0084	0.0088	0.0079	0.0079
Candy	0.0042	0.0042	0.0047	0.0047
Candy	0.0017	0.0019	0.0017	0.0017

[1] Sulphur dioxide added as sulphite: Sugar, 0.0050 part per 100
Flour, 0.0050 part per 100
Starch, 0.0025 part per 100

SULPHUR DIOXIDE FOUND.
Parts per 100.

	Official method.		Modified method.	
Prepared samples.	Direct titration.	After oxidation.	Direct titration.	After oxidation.
Candy	0.0120	0.0120	0.0126	0.0126
Peas, fresh, average 5	0.0002	0.0002	0.0000	0.0000
Peas, same processed	0.0002	0.0008	0.0000	0.0000
Peas, canned, average 5	0.0003	0.0008	0.0000	0.0002
Peas, canned, average 5	0.0004	0.0011	0.0002	0.0004
String beans, white, fresh	0.0000	0.0003	0.0000	0.0000
String beans, same processed	0.0002	0.0007	0.0000	0.0002
String beans, yellow, fresh	0.0001	0.0002	0.0000	0.0000
String beans, same processed	0.0001	0.0005	0.0000	0.0002
Cabbage, fresh	0.0002	0.0003	0.0000	0.0000
Cabbage, same processed	0.0002	0.0011	0.0000	0.0003
Green peppers, fresh	0 0000	0.0002	0.0000	0.0002
Green peppers, same processed	0.0002	0.0006	0.0000	0.0003
Cauliflower, fresh	0.0000	0.0000	0.0000	0.0000
Cauliflower, same processed	0.0000	0.0003	0.0000	0.0002
Rhubarb, fresh	0.0000	0.0000	0.0000	0.0000
Rhubarb, same processed	0.0001	0.0002	0.0000	0.0000
Onions, fresh	0.0000	0.0004	0.0000	0.0002
Onions, same processed	0.0002	0.0008	0.0000	0.0006
Cucumbers, fresh	0.0000	0.0000	0.0000	0.0000
Cucumbers, same processed	0.0000	0.0001	0.0000	0.0000
Okra, fresh	0.0000	0.0000	0.0000	0.0000
Okra, same processed	0.0000	0.0000	0.0000	0.0000
Processing solution[1]	0.0000	0.0000	0.0000	0.0000

The figures obtained on the prepared samples, indicate that carrying out exactly the Official method of distillation is not sufficient to drive over all the sulphur dioxide contained in the samples. The character of the products influencing the amount of sulphur dioxide held back, from 10 per cent. for sugar to 26 per cent. for flour, the loss due to incomplete distillation in the modified method being 4 per cent. for flour and none for the other two products. With the exception of candies, the modified method gives lower results, although the distillation is more complete.

When examining cereals or other products very high in starch, both methods must be modified by either increasing the amount of acid and water or decreasing the amount of the material used, as otherwise the mass becomes semi-solid or pasty. The vegetables enumerated were obtained in the open market. The processing consisted in taking the washed vegetables, breaking or crushing into small pieces, when necessary, and then placing 500 grams into Mason jars, pouring on 500 cc. of the hot processing solution, hermetically sealing the jars, and then placing into a boiling water bath for one hour. After cooling, the whole mass was pulped and of this 200 grams, representing 100 grams of the vegetable, taken for each determination, adding in each case 100 cc. water using the official method and 200 cc. water using the modified method, the amount of distillate being

[1] Processing solution: sugar 5 parts, salt 1 part, and water 100 parts.

exactly 50 cc. for the official method and not less than 400 cc. for the modified method. In making the direct titration tests for both methods, the distillates were caught in an alkaline solution, and after acidifying with phosphoric acid, titrated with 1/100 normal iodine solution and starch paste as the indicator. When sulphur dioxide was determined by oxidation, including all other volatile sulphur compounds, the distillate was caught in an iodine solution to which a few drops of bromine had been added. This was boiled over a direct flame until colorless and total sulphur compounds precipitated with barium chloride and weighed as barium sulphate. The apparatus was always filled with carbonic acid gas, generating same in the steam boiler from bicarbonate of soda and phosphoric acid.

It was found that results obtained in the direct distillation, official method, differed, as the amount of the distillate was increased above 5 cc. Up to a certain, not constant point, a slight increase was obtained by both direct titration and by oxidation. Going beyond that point, the amounts found by direct titration of the excess of iodine, were always above those found by oxidation, showing conclusively that non-sulphur decomposition products were distilled, due to further decomposition and that these materially affected the back titration of the excess of iodine. This was further confirmed by the fact that the results obtained when distilling directly into an iodine solution were greater than the actual sulphur dioxide calculated from the barium sulphate precipitate of the same solution and the results obtained by direct distillation into iodine were always higher than those obtained when distilling into an alkaline solution and titrating the sulphur dioxide liberated on acidifying. The amount of sulphur dioxide found by oxidation of a larger quantity of distillate being less than the amount found on titrating the distillate direct, using the larger amount for the determination of sulphur dioxide by precipitation.

Volatile compounds, such as essential oils, ethers and oxides, which combine with iodine, effect the accuracy of both methods, but are partly eliminated in the modified method, depending upon their solubility in the alkaline solution into which they are distilled. Such volatile compounds often can be separated by boiling the alkaline distillate, then cooling, diluting to original bulk and, after acidifying, titrating the sulphur dioxide remaining in the solution.

No appreciable error is introduced by boiling the alkaline distillate.

The comparative results obtained in the determination of sulphur dioxide and its compounds in food products by the official and modified methods, justifies the conclusions that:

I—The Official method for sulphur dioxide, sulphites or sulphurous acid should be changed so as to eliminate the possibility, as has occurred in actual practice, of food products being condemned and rejected by food officials and private persons as not meeting the requirements of Federal and State Food Acts, on account of the presence of sulphur dioxide or its compounds, examined according to the Official method, but containing no added sulphur compounds.

II—Traces of sulphur dioxide or its compounds, or what is found as such, should be ignored as well for all food products as specifically only for meat and meat products.

THE DETERMINATION OF ESSENTIAL OIL AND ALCOHOL IN FLAVORING EXTRACTS.

By Julius Hortvet and Rodney Mott West.

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Little is to be found in chemical literature relating to the determination of either essential oil or alcohol in flavoring extracts. With the exception of extracts of lemon and orange, this field of investigation[1] appears to have been in great measure neglected, and it is doubtful whether prior to 1899 any successful attempts had been made to devise methods of making these determinations. In a paper entitled "Lemon Flavoring Extract and its Substitutes,"[2] published about ten years ago, A. S. Mitchell gave two methods for the determination of lemon oil. These methods, somewhat revised, were later adopted as provisional by the Association of Official Agricultural Chemists.[3] In 1901, Winton and Ogden[4] applied the polariscopic method, as described by Mitchell for lemon extract, to extract of orange, establishing the factor 5.3 for the calculation of the per cent. of oil by volume from the reading on the Ventzke sugar scale. With reference to miscellaneous flavor-

[1] Only those flavoring extracts which consist chiefly of an alcoholic solution of an essential oil are considered in this paper.

[2] *Jour. Am. Chem. Soc.*, **21**, 1132 (1899).

[3] Bull. **107**, Bureau of Chemistry, U. S. Dept. of Agr., pp. 156–161.

[4] Report Conn. Agr. Expt. Sta., 1901, Part II, p. 176.

ing extracts, the following general statement by A. E. Leach[1] appears to have been accepted without serious question: "In the case of extracts of oils, it is generally practicable to separate the oil for examination by the centrifuge, as in the precipitation method of Mitchell, and to estimate the same directly as described on page 742 (Mitchell's method *b*), when the specific gravity of the oil in question is less than water. In the case of such oils as clove, wintergreen and cassia, where the specific gravity is greater than water, it is necessary to add salt to the extract before centrifuging to cause separation of the oil." The same author also describes an extraction method for the determination of oil of almond in almond extract.[2] An article entitled "The Precipitation Method for the Estimation of Oils in Flavoring Extracts and Pharmaceutical Preparations,"[3] published during the present year by C. D. Howard, so far as known, completes the literature on this subject up to the present time. A discussion of the general method described by Howard will be given at a later stage in the course of this article. In the case of extracts other than those of orange and lemon, many food chemists appear to have satisfied themselves with results obtained from the estimation of alcohol and the detection of essential oil by means of dilution with water. The following statement fairly illustrates some of the prevailing methods: "Extracts of clove, peppermint, orange and almond, which are of standard strength, will on dilution with water become turbid, due to the precipitation of the oil. The true extract will contain enough alcohol so that it will burn, but those below standard will not do so." It appears from published analyses, chiefly in the reports of several state food laboratories,[4] that the solids and ash of extracts have been relied upon to some extent as criteria of purity, but it is uncertain from the analyses themselves whether such results were obtained merely for the purpose of detecting the addition of sugar or glycerine. However, since the solids were determined by drying to constant weight at 100° C., it is readily seen that the results could be of little or no practical value in connection with the determination of either the oil or alcohol content of an extract.

The adoption of standards for flavoring extracts by the joint Committee on Food Standards of the Association of Official Agricultural Chemists and the Association of State and National Food and Dairy Departments, followed by the legal adoption of these standards by several of the states, has rendered it imperative that further attempts be made to perfect methods whereby the amount of essential oil in any of the common extracts used for food flavoring purposes may be readily and accurately determined. After numerous preliminary trials in this laboratory with methods which have heretofore been proposed, it became very evident that it would be difficult if not impossible to devise a single method that would be applicable to all extracts. Very few of the volatile oils used in making the common flavoring extracts are optically active. Only in the case of the oils of lemon and orange peel and celery seed are the rotations sufficiently high and constant to render possible a practical method based on the polarization of the extract. All of the oils, with the exception of oil of bitter almond, may be more or less completely precipitated by the addition of water to the acidified alcoholic solution, but only about half of them can be separated sufficiently to afford a method of any practical value. The reasons for the failure of the precipitation method in so many instances are at once apparent when the differences in chemical composition and physical properties of the various oils are considered. For instance, oil of bitter almond, which is essentially benzaldehyde, has a solubility in water of one part in three hundred, while a one per cent. solution can be made with 20 per cent. alcohol. The addition of water in any amount to such a solution will not cause the least cloudiness. In both cinnamon and cassia oils the principal constituent is cinnamic aldehyde, also fairly soluble in dilute alcohol, and in extracts where either of these oils is present in amount above two per cent. the precipitation method gives only about fifty per cent. of the total oil. Oils of lemon, orange and nutmeg, on the other hand, consisting very largely of terpenes insoluble in dilute alcohol and chemically passive in respect to the dilute acid used in the precipitation method, are all very easily precipitated. It has therefore been deemed necessary to devise for each kind of extract, or for each class of extracts, a special method for the determination of the essential oil. Any such method should be applicable not only in the presence of very low as well as very high percentages of oil, but also

[1] Food Inspection and Analysis, A. E. Leach, p. 747.

[2] Food Inspection and Analysis, A. E. Leach, p. 750.

[3] *Jour. Am. Chem. Soc.*, **30**, 1908, 608.

[4] State Dairy and Food Commission Reports: Ohio, 1896; Michigan, 1903; Illinois, 1905, 1906, 1907; Inland Revenue Department, Ottawa, Canada, Bull. **89**, p. 13 (1903).

in the presence of excessive amounts of alcohol, sugar or glycerine, and the results should not be vitiated by the presence of any of the common adulterants. Also, it is very desirable that the oil should be separated in such condition that tests for impurities may be carried out directly upon it. In many cases it has been found that the condition necessary to a satisfactory method are most nearly reached by precipitation; hence this method has been tried wherever possible. A modification of the present Official precipitation method has been found to work acceptably with extracts of lemon, orange, peppermint, nutmeg and wintergreen. Two other general methods have also been found satisfactory: one consists in the extraction of the oil by means of a volatile immiscible solvent, the other in the determination of the principal constituent of the oil; the first has been found to work acceptably with extracts of clove, cinnamon, cassia and rose, the second with extracts of almond and wintergreen.

For the purpose of preliminary work, alcoholic solutions were prepared containing in each instance an amount of oil sufficient to make an extract which would comply with the standard found in Circular No. **19** of the United States Department of Agriculture. These solutions were then subjected to examination according to the various methods for determining volatile oil.

Almond Extract.—An extract of almond was prepared, containing one per cent. by volume of oil of bitter almond, free from hydrocyanic acid, in approximately 25 per cent. alcohol. It was found that any amount of water, whether acid or neutral, or saturated with salt, could be added to the extract without causing the precipitation of even the slightest trace of the oil. Attempts at extraction with an immiscible solvent proved equally fruitless, owing principally to the rapid partial oxidation of the oil to benzoic acid during the evaporation of the solvent. All attempts to conduct the evaporation in such a manner as to complete the oxidation quantitatively resulted in loss, spontaneous evaporation giving rise to loss of aldehyde while evaporation at higher temperatures caused an additional loss of benzoic acid. The method given by Leach is open to the same objections, the long and tedious process of removing the alcohol holding a doubtful advantage over the method in which alcohol can easily be removed by washing the ether with a few changes of water. Bitter almond oil, free of hydrocyanic acid, is substantially benzaldehyde, the amount of the latter ingredient ranging ordinarily from 90 to 95 per cent. Hence it occurred that a determination of the benzaldehyde content of an extract would afford the most practicable means of ascertaining the amount of oil present. The customary aldehyde methods were tried, both the bisulphite of soda method[1] and the neutral sulphite method[2] resulting in indifferent success. Any reasonable concordance in results seemed to be impossible and approximately only from 85 to 90 per cent. of the actual oil present could be obtained. Such results were without doubt at least partially due to the presence of alcohol since in the neutral sulphite method, alcohol, even in small amounts, prevents the formation of starch-iodide, while the high acetaldehyde content of commercial alcohol would in any case vitiate results obtained by a method based on the determination of the total aldehyde. Considering also the ease with which benzaldehyde is oxidized, it is obviously inaccurate as well as unfair to estimate the oil merely from the aldehyde, when a considerable amount of the oil which was originally added may have been converted to benzoic acid subsequent to the manufacture of the extract. Furthermore, a correction based on the acidity of such an extract would be too superficial to be of value, since commercial alcohol is always decidedly acid in reaction. It has become necessary, then, for factory control work, as well as for general analytical purposes, that a method be devised whereby the benzaldehyde content of an extract at the time of manufacture may be fairly determined. It appeared to be practicable to base a calculation of the original oil on the benzoic acid obtained after complete oxidation of the aldehyde. With this plan in mind, various methods were tried, aiming at a complete oxidation of the oil without loss by volatilization. After several trials with various oxidizing agents, including oxygen, potassium bichromate and potassium permanganate, hydrogen peroxide in alkaline solution was found to be the most satisfactory. Attempts were made to oxidize in a standard alkaline solution and titrate the excess of alkali, but owing to the indeterminate increase of acidity, the results were far too high and non-concordant. Such results were in all probability due to the oxidation of the ethyl alcohol in the extract. The hydrogen peroxide was submitted to a blank titra-

[1] Sutton, "Volumetric Analysis," ninth edition, p. 371.
[2] S. S. Sadtler, *Jour. Soc. Chem. Ind.*, **23**, 303 (1904)

tion, but even with the correction thus afforded, the results were still unsatisfactory. Recourse was then had to extraction with ether as a means of obtaining the benzoic acid in a pure condition. The method finally adopted is as follows:

Ten cc. of the extract are measured out by means of a pipette into a 100 cc. flask, ten cc. of approximately a 10 per cent. solution of sodium hydroxide and 20 cc. of a 3 per cent. solution of hydrogen peroxide added, the flask covered with a watch-glass and placed on a water oven. Oxidation begins almost immediately and should be continued from five to ten minutes after all odor of benzaldehyde has disappeared. Usually from twenty to thirty minutes will be found sufficient. If nitrobenzol be present, it will be indicated at this point by its odor. When the oxidation of the aldehyde is complete, the flask is removed from the water-oven, the contents transferred to a separatory funnel, rinsing off the watch-glass into the funnel, 10 cc. of a 20 per cent. solution of sulphuric acid added, and the contents of the funnel cooled to room temperature under the water tap. The acid solution is extracted with three portions of ether, using in succession 50, 30 and 20 cc. A fourth extraction showed no trace of benzoic acid. The extracts are combined in another separatory funnel and washed with distilled water until the wash water shows no trace of sulphate on acidifying with hydrochloric acid and testing with barium chloride. Two portions of water of from 25 to 30 cc. each should be sufficient to remove all of the sulphuric acid. The ether extract is transferred to a wide-necked flask and the ether evaporated by placing the flask on a water oven. When the volume of the ether has been reduced to about 5 cc., the flask is removed from the oven and the evaporation completed spontaneously. When all of the ether has evaporated from the benzoic acid, the sides of the flask are washed down and the crystals dissolved by means of 95 per cent. alcohol which has been made neutral to phenolphthalein with tenth-normal sodium hydroxide. The solution of benzoic acid is diluted with about an equal volume of water and the acid titrated with tenth-normal sodium hydroxide, using phenolphthalein as indicator.

$$\frac{\text{cc. of N/10 NaOH} \times 0.01061 \times 10}{1.045} = \text{per cent.}$$

of benzaldehyde by volume. If desired, the ether extract may be filtered through a dry filter into a tared flask, the ether evaporated as before, the residue dried in a desiccator over night and weighed as benzoic acid.

$$\frac{\text{Weight of acid} \times 0.869 \times 10}{1.045} = \text{per cent. of}$$

benzaldehyde by volume. The volumetric and gravimetric results are not found to differ by more than a few hundredths of one per cent. The method is satisfactory,[1] giving concordant results irrespective of the per cent. of alcohol or oil which may be present. Also, results by this method are not in the least vitiated by the presence of hydrocyanic acid, glycerine or sugar. If nitrobenzol be found to be present, it may be removed by the method given by Leach[2] before attempting the determination of the aldehyde. The fact that benzaldehyde constitutes not more than from about 90 to 95 per cent. of almond oil somewhat detracts from the value of the method, but, on the other hand, as the necessary correction will be seen to be fairly constant, this objection is of far less moment than would at first appear.

Cinnamon, Cassia and Clove Extracts.—A two per cent. by volume solution of each of these oils in approximately 65 per cent. alcohol was prepared for the preliminary work. As the specific gravity of each oil averages about 1.050 at 25° C., the precipitation method recommended by Leach was attempted. Other heavy liquids, such as dilute sulphuric acid (1 : 1) and a saturated solution of copper sulphate, were also tried. With none of these precipitants, however, were the results satisfactory. This was true especially in the case of clove oil which seemed to be acted upon chemically and dissolved by the salt as well as by the acid. Only very small percentages of the total oil were found to be recoverable under the best conditions. A method similar to the one described for the determination of benzaldehyde was then tried with cinnamon and cassia extracts. By this method the cinnamic aldehyde was oxidized to the corresponding acid by means of hydrogen peroxide in alkaline solution, the solution acidified, extracted with ether, the ether evaporated and the residue weighed as cinnamic acid and calculated to cinnamic

[1] This method may be used for the determination of benzaldehyde in almond oil by weighing out 0.1 to 0.2 gram of oil, dissolving in about 10 cc. of alcohol and continuing as in the method for an extract. To determine the amount of the aldehyde actually present as such in the oil, a few cc. of oil should be dissolved in a little carefully neutralized alcohol and titrated with standard alkali. The acidity thus obtained calculated to benzoic acid is subtracted from the total acid before calculating to benzaldehyde.

[2] Food Inspection and Analysis, A. E. Leach, p. 750.

aldehyde.[1] Very concordant results were obtained, but the aldehyde content of these oils is too small to make the method practicable. There remained then the method of extraction of the volatile oil, using ether as the immiscible solvent. Ten cc. of the sample were diluted with water and extracted with three portions of ether. In the earlier experiments the ether was evaporated without previous washing in a tared dish and the residue weighed. It was found, however, after driving off the ether that there still remained a considerable amount of alcohol which could only be removed with difficulty and with considerable loss of oil. To surmount this difficulty, it was found sufficient to wash the combined ether extracts with two portions of distilled water of from 25 to 30 cc. each. By this means practically all of the alcohol was removed and the loss of volatile oil was found to be negligible. The greatest difficulty, however, consisted in finding a method for the evaporation of the solvent which would cause the least possible loss of oil. Heating on the water oven until only a few cc. of ether remained, then finishing the evaporation spontaneously, resulted in too great a loss of oil, while, strangely enough, spontaneous evaporation from the start caused a still greater loss. Rapid evaporation of the ether under diminished pressure was found to lower the temperature of the water to the congealing point, thus making it possible to obtain a weighable residue only after a prolonged drying which resulted in an apparent loss of volatile oil. Yet fairly good results were obtained by this method providing the ether extract was previously dried. Shaking for a few minutes with calcium chloride and filtering through a dry filter was found to dry the ether sufficiently in the case of extracts of cinnamon and cassia. Clove oil, however, was found to combine with the calcium chloride, as well as to react chemically with all of the common dehydrating agents, thus making reliable results impossible. Since the best results had been so far obtained in those determinations in which the ether was boiled off as rapidly as possible under diminished pressure, it appeared possible that good results might be obtained by rapid evaporation at higher temperatures in the open air, with the additional advantage of removing the water remaining in the ether. That is to say, the loss in volatile oil seemed to be somewhat in proportion to the time taken for the evaporation of the solvent, irrespective of temperatures well below the point at which the oil itself would distil. Surprising as it may seem, the best results were obtained by evaporating the ether from a wide mouth flask placed in direct contact with the live steam from a boiling water bath. The boiling ether kept the temperature of the solution below 40 to 45° C., while the few minutes required for the complete removal of the solvent gave little time for the evaporation of the essential oil. In the case of oil of cinnamon, better results were obtained when the ether extract was first dried by shaking with a little calcium chloride. With cassia and clove extracts, however, the results were exceedingly good when the evaporation was carried out without previous drying of the ether. This method requires considerable care in manipulation and the following details should be closely adhered to.

[1] This method appears to be a practicable one for the determination of cinnamic aldehyde in oils of cinnamon and cassia, but as yet no data have been obtained to establish its reliability.

Ten cc. of the extract are transferred to a separatory funnel, 50 cc. of water added, and the mixture extracted with three portions of ether, using in succession 50, 30 and 20 cc. The combined ether extracts are washed with two changes of distilled water, using each time 25 to 30 cc., and filtered through a dry filter into a wide mouth flask, washing out the funnel and filter with a little ether. In the case of an extract of cinnamon, the ether extract before filtering is transferred to a 150 cc. flask, shaken for a few minutes with some granulated calcium chloride, then filtered through a dry filter in the manner described above. The ether is evaporated off as rapidly as possible on a boiling water bath until only a few drops remain. At this point the flask is removed from the water bath and rotated rapidly for a few minutes, spreading the residue over the sides of the flask. The rapid evaporation of the remaining ether cools the flask to near room temperature. When the odor of ether has disappeared, the flask is stoppered and weighed. In the case of cassia and clove oils, where the ether extract is not first dried with calcium chloride, a slight cloudiness gathers on the flask as the last traces of ether disappear, due to the presence of a little moisture. In such case, the flask is allowed to stand on the balance pan until the film of moisture disappears (requiring not longer than two or three minutes), then stoppered and weighed.

$$\frac{\text{Weight of oil} \times 100}{10 \times 1.050} = \text{per cent. of oil by volume.}$$

The oil thus extracted may be used for examination

as to purity by means of the refractometer. It may also be tested by dissolving a portion in a little alcohol and adding a drop of ferric chloride. Cinnamon oil will give a green coloration, cassia a brown and clove a deep blue.

Rose Extract.—On account of the small percentage of oil of rose which is commonly employed in making the extract, as well as the fact that the oil is not readily separated from solution by dilution with water, no attempts were made to apply the precipitation method. Furthermore, oil of rose is comparatively optically inactive and of such composition that the choice of a method appeared to be narrowed to that of extraction by means of an immiscible solvent. Accordingly, an extract was prepared by dissolving 0.4 cc. of oil of rose in 100 cc. of approximately 80 per cent. alcohol. A number of determinations were attempted, resulting finally in a method in some respects similar to the foregoing described for extracts of cinnamon and clove. It was, however, not found advisable to wash the ether solution with water or to apply the method of rapid evaporation over a water-bath. The method is as follows:

Twenty cc. of the extract are measured into a separatory funnel, 50 cc. of water added, the solution thoroughly mixed, acidified with 1 cc. of hydrochloric acid (1 : 1), and extracted with three portions of ether, using each time 20 cc. The combined ether extracts are transferred to a 150 cc. flask, shaken for a few minutes with some granulated calcium chloride, allowed time to settle to a clear solution, then decanted through a dry filter into a flat bottom glass dish previously weighed together with a cover glass. The calcium chloride and filter are twice washed with 10 cc. of ether and the washings added to the contents of the dish. The dish is covered, placed in a vacuum desiccator over sulphuric acid and allowed to remain until all traces of ether and alcohol are removed, then weighed, again placed in the desiccator at ordinary pressure for one hour and weighed again. The last operation is repeated if necessary and the weight recorded when practically constant. The final weight divided by 0.86 and multiplied by 5 gives the per cent. of oil of rose by volume.

Lemon, Orange, Peppermint and Nutmeg Extracts.—According to chemical literature, menthol, the chief constituent of oil of peppermint, is found in the oil in amounts varying from approximately 40 to 90 per cent. Hence, any attempts to base a calculation of the amount of oil in extract of peppermint on the determination of the menthol content would be likely to yield unsatisfactory results. With oil of nutmeg the case is similar, the chief constituent of the oil being pinene which could not readily be determined in a solution containing the oil in amounts commonly employed in making the extract. It is apparent, also, from published data that the optical rotation of neither oil of peppermint nor oil of nutmeg could afford a successful polarimetric method. Preliminary trials, however, with the Official precipitation method for lemon extract were found to give satisfactory results. In the case of a peppermint extract made to contain 3 per cent. of the oil a correction of only 0.2 per cent. was found necessary, while in the case of a nutmeg extract made to contain 2 per cent. of oil scarcely an appreciable correction was required. It was considered, however, that for the purpose of further examination of the separated oil as well as for the alcohol determination, the amount of sample taken in the Official method is inadequate; hence it was thought that it might be desirable to devise an apparatus whereby there might be employed a larger sample, thus avoiding some of the usual difficulties and at the same time possibly lessening the percentages of error in the results. The larger tube, shown in Fig. 1, is similar in shape to the Babcock milk test bottle, but is of 150 cc. capacity to the beginning of the graduations on the stem. The stem is graduated to read to tenths of one per cent., the divisions being based on the use of 50 cc. of sample in the determination. As the common form of centrifuge is obviously not suitable for carrying the larger test bottles, recourse was had to the Bausch and Lomb precision centrifuge which was found to be admirably adapted to the requirements. A pair of special holders, suitable for carrying the bottles, is provided with the machine. The following method was found to work satisfactorily with extracts of lemon, orange, peppermint and nutmeg.

Fifty cc. of the extract are measured into the test bottle, the temperature noted, 1 cc. of hydrochloric acid (1 : 1) added, then water (previously heated to 60° C.) poured in to near the beginning of the stem. The bottle, closely stoppered with a small cork, is allowed to stand in water at 60° C. for about 15 minutes, occasionally giving it a twisting motion to facilitate the separation of the oil, then run 10 minutes in the centrifuge at a speed of about 800 revolutions per minute. A little hot water is added cautiously until the oil rises

above the 150 cc. mark and the bottle again run in the centrifuge 10 minutes. In case the separation does not appear to be satisfactory, or if the liquor is not clear, good results are obtained by cooling the bottle and contents to about 10° C., then running in the centrifuge an additional 10 minutes. Occasionally a light oil will be found which does not rise completely into the stem of the bottle. In such a case good results are secured by using salt solution (1 : 1), previously heated to 60° C., instead of water. The per cent. of oil is measured by means of a pair of dividers, from the extreme bottom to the top of the column. The oil may then be removed by means of a small pipette and a piece of absorbent paper and the remaining liquor used in the alcohol determination.

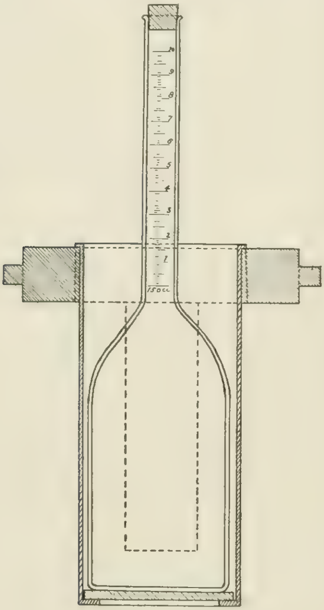

Fig. 1.

Wintergreen Extract.—(*a*) The precipitation method was also found to be applicable to extract of wintergreen, but, owing to the fact that oil of wintergreen has a specific gravity of about 1.18, the tube described in the foregoing method could obviously not be used. A tube was therefore constructed for heavy oils, as shown in Fig. 2. The capacity of the tube is about the same as that of the tube for light oils and the stem is also graduated to tenths of one per cent., based on a 50 cc. sample. This tube may also be fitted by means of a cork cushion into one of the special holders provided with the precision centrifuge. The method is essentially the same as the one given for light oils, omitting the heating in the water-bath previous to running in the centrifuge. At the close of the first 10 minutes' run the tube and contents are cooled to 10° C. and the remainder of the operation is completed as described. The alcohol-water liquor is blown out into a test bottle made for light oils, the residual liquor rinsed out with a little water and the solution set aside for the alcohol determination. The remaining oil is then removed and examined for purity.

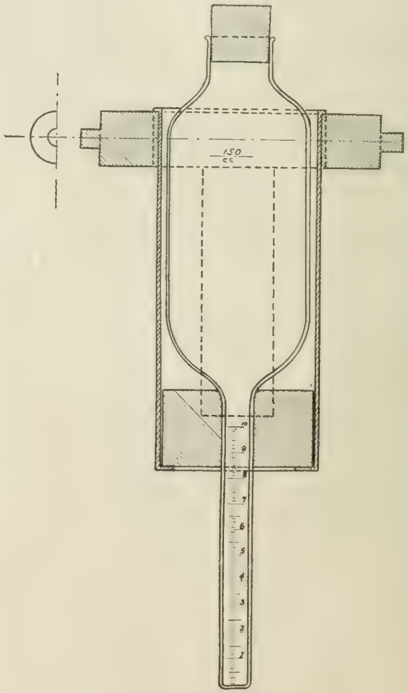

Fig. 2.

(*b*) Methyl salicylate constitutes about 99 per cent. of oil of wintergreen; hence a determination of this constituent in a wintergreen extract would give substantially the amount of oil. The following method was found to give good results.

Ten cc. of the extract are measured into a 100 cc. beaker, 10 cc. of a 10 per cent. solution of potassium hydroxide added, and the mixture heated over a boiling water-bath until the odor of oil of wintergreen has disappeared and the liquor reduced to about one-half its original volume. A 10 per cent. solution of hydrochloric acid is added to distinct excess and the liquor cooled. The salicylic acid is extracted with three portions of ether, using in succession 40, 30 and 20 cc., the combined ether extracts poured through a dry filter into a weighed dish, the filter washed with an additional 10 cc. of ether, and the combined filtrate evaporated slowly at about 50° C. The crystals are dried one hour in a desiccator and weighed.

$$\frac{\text{Weight of salicylic acid} \times 1.101 \times 10}{1.18} = \text{per}$$

cent. of oil of wintergreen by volume. The preliminary work having been completed, three extracts were prepared from each kind of essential oil. One was made to conform to the standard given in Circular No. **19** of the United States Department of Agriculture and contained approximately the per cent. of alcohol required to dissolve the oil, one was made deficient in oil, and one was made to contain oil in excess of the standard and much higher than the necessary per cent. of alcohol. These solutions were then submitted to analyses according to the methods which have been described. The results are shown in Table I.

TABLE I.—RESULTS OF THE DETERMINATION OF VOLATILE OILS IN FLAVORING EXTRACTS.

(Results expressed as per cent. by volume.)

	Composition of extract.		By extraction.		By precipitation		By chief constituent.	
Kind of extract.	Per cent. alcohol used.	Per cent oil.	Per cent. oil found.	Per cent. total oil found.	Per cent. oil found.	Per cent total oil found.	Per cent. oil found.	Per cent. total oil found.
Almond	26.40	0.50	.....	......	....	......	0.468	93.60
	26.40	1.00	.....	......	....	......	0.937	93.70
	80.12	1.50	.....	......	....	......	1.416	94.40
Cinnamon	68.72	1.00	0.982	98.20	....	......	.....	.....
	68.72	2.00	1.945	97.25	....	......	.....	.....
	94.92	3.00	2.941	98.03	....	......	.....	.....
Clove	84.67	1.00	0.991	99.10	....	......	.....	.....
	84.67	2.00	2.004	100.20	....	......	.....	.....
	94.92	3.00	3.005	100.17	....	......	.....	.....
Cassia	68.72	1.00	0.995	99.50	....	......	.....	.....
	84.67	2.00	1.998	99.80	....	......	.....	.....
	94.92	3.00	2.962	98.73	....	......	.....	.....
Lemon	84.67	3.00	.....	......	2.90	96.67	.....	.....
	94.92	5.00	.....	......	4.90	98.00	.....	.....
	94.92	7.00	.....	......	6.80	97.14	.....	.....
Orange	84.67	2.00	.....	......	2.00	100.00	.....	.....
	94.92	5.00	.....	......	5.00	100.00	.....	.....
	94.92	7.00	.....	......	6.85	97.86	.....	.....
Nutmeg	84.67	1.00	.....	......	0.90	90.00	.....	.....
	84.67	2.00	.....	......	1.85	92.50	.....	.....
	94.92	4.00	.....	......	3.75	93.75	.....	.....
Wintergreen	68.72	1.50	.....	......	1.15	76.67	1.460	97.53
	68.72	3.00	.....	......	2.65	88.33	2.930	97.67
	94.92	5.00	.....	......	4.60	92.00	4.836	96.72
Peppermint	84.67	1.00	.....	......	1.15	76.67	.....	.....
	84.67	3.00	.....	......	2.78	92.67	.....	.....
	94.92	5.00	.....	......	4.75	95.00	.....	.....
Rose	80.00	0.40	0.360	90.00	....	......	.....	.....
	85.00	0.45	0.410	91.11	....	......	.....	.....

On examination of the table it will be seen that under the best conditions small corrections should be applied to the results in the case of most of the extracts. This is particularly true with extracts of cinnamon, peppermint and nutmeg. However, the errors will be found to be fairly constant, provided that the conditions under which the methods are carried out are kept as uniform as possible. It would be well for each operator to work on one or two known solutions according to each method and in that way determine for himself and for the conditions under which he works just what per cent. of oil he is able to recover. In thus establishing his own factors for the corrections, the personal

equation inherent in each method will be largely eliminated.

The precipitation method described by Howard for the "estimation of oils in flavoring extracts and pharmaceutical preparations" was subjected to a number of preliminary trials on extracts made in this laboratory and was found to give results which in several cases were apparently satisfactory. Further experience, however, disclosed serious defects in the method. This occurred especially with almond extracts, in which ten determinations made strictly according to the prescribed conditions gave at best only a small proportion (never exceeding 0.15 per cent.) of the actual oil present. In some cases the results were nil, the oil having been apparently completely lost during the process. When the method was applied to some of the other extracts the results were more satisfactory, the reading of the oil column giving the exact per cent. of oil in several instances. At times, however, the results were either too high or too low, the variations occurring under seemingly identical conditions. A little consideration led to the conclusion that the method is faulty in several particulars. It seemed incomprehensible that a one-half cubic centimeter of chloroform could be sufficient to remove from a 10 cc. sample of an extract all of the essential oil, even after the oil had been partially precipitated by means of water. Dilution of 10 cc. of a 90 per cent. alcohol to at most 40 cc. (the average capacity of a Babcock bottle) still leaves a solution containing approximately 20 per cent. of alcohol. Particularly in the case of extracts whose oils are fairly soluble in dilute alcohol, a 20 per cent. alcohol solution might be expected to retain a considerable amount of the oil. In arguing the complete extraction of the oil by his method, Howard states: "All the oil is dissolved by the chloroform, while the latter in saturating the water, apparently serves to displace any appreciable trace of oil, otherwise retainable by the alcohol-water mixture." The fact that the water becomes saturated with the chloroform arouses the suspicion that some of the oil may be retained in solution by the chloroform water mixture. During the evaporation of the chloroform the odor of the oil is very easily detected, and at the end of the prescribed one minute period of heating in contact with steam it is seldom that the odor of chloroform is not plainly evident. It is also conceivable that in certain instances a small amount of the oil may be taken up whenever dilute sulphuric acid is used for the purpose of raising the oil into the graduated neck of the bottle. Furthermore, experience has led to the belief that there is a greater loss of volatile oil during the evaporation of the chloroform than might be suspected, particularly in the case of such volatile oils as almond and cinnamon.

In order to decide some of these questions the various portions obtained in the Howard process were assayed separately for the per cent. of essential oil which they might contain. For this purpose such methods were used as have been found to be best suited to the oils in question. The results of these determinations are shown in Table II. Referring to the Table, "A" is the solution which was drawn off with the aspirator from the Babcock bottle after the first run in the centrifuge. After the operation was finished, the contents of the bottle were poured into a small separatory funnel, the oil allowed time to separate and the lower liquor run out as completely as possible and assayed as "B." The bottle was then rinsed out with ether and the rinsings added to the oil in the separatory funnel, constituting portion "C." The results under "D" were obtained by difference and represent the loss of oil during the evaporation of the chloroform. In the determinations made on the almond extracts the amounts of oil obtained were so very small that it became necessary to determine the proportions of oil present in portions "B" and "C" in one operation. In all case where deemed necessary, qualitative tests were applied for the purpose of identifying the oil obtained.

The results shown in the table are significant. While in general the results by the Howard method are apparently correct in many instances, a closer examination will reveal the fact that the actual essential oil obtained seldom approximates to the amount contained in the sample. It is evident that a considerable amount of the oil is retained by the alcohol-water solution, also that a small amount is lost in the solution added to raise the oil into the graduated neck of the test bottle. The fact that in all cases only a portion of the column read off is shown to be essential oil is adequate evidence that various amounts of chloroform are retained in the process and erroneously included in the results. In other words, the method is one involving oppositely occurring errors that may or may not compensate in the results obtained.

The determination of alcohol in flavoring ex-

tracts involves some peculiar difficulties which can best be referred to by giving a description of some of the methods which have heretofore been accepted. The method given by Allen[1] for the determination of alcohol in tinctures, modified so as to apply also in the presence of essential oils, is substantially as follows:

Fifty cc. are made up to 350 cc. by the addition of water, the liquid clarified by the addition of a few drops of a strong solution of calcium chloride followed by some sodium phosphate, made up to 400 cc., filtered through a dry filter, and 250 cc. of the filtrate distilled. The distillate is made up to 250 cc. by the addition of water and the density observed. The corresponding percentage of alcohol is multiplied by 8 to obtain the per cent. of alcohol in the original tincture.

The present Official method[2] involves the same principle, differing only in the amount of dilution and in the use of magnesium carbonate in place of calcium phosphate for removing the precipitated oil. In these methods, as in others which are essentially similar in all respects, the oil is at best only more or less imperfectly removed, a serious defect which has apparently failed to attract general attention. Thorp and Holmes[1] remove the oil by extraction with an immiscible solvent, proceeding as follows:

Twenty-five cc. of the sample are taken, 100 cc. of water added, the mixture saturated with common salt and shaken for 5 minutes with 70 cc. of petroleum ether (b. p. under 60° C.). The aqueous layer is then drawn off and the petroleum ether washed twice with 25 cc. of saturated salt solution. These washings are added to the original aqueous solution and the whole distilled slowly until 100 cc. of distillate is obtained. The alcoholic content of the distillate is multiplied by four to obtain the per cent. of alcohol in the extract.

Table II.—Results of the Examination of Howard's Method.

(Results expressed by volume.)

Kind of extract.	Composition of extract. Per cent. alcohol.	Per cent oil.	Per cent. oil by Howard's method.	Assay of "A." Oil found.	Per cent. total oil found.	Assay of "B." Oil found.	Per cent. total oil found.	Assay of "C." Oil found.	Per cent. total oil found.	Per cent. oil in column.	Per cent chloroform in column.	"D." Oil.	Per cent. total oil.
Almond	26.14	1.00	0.15	0.0278	27.80	......	.....	0.0596	59.60	.....	.....	0.0126	12.60
	78.92	1.50	0.15	0.0397	26.47	......	.....	0.0795	53.00	.....	.....	0.0308	20.53
Cassia	68.03	1.00	1.20	0.0153	15.30	0.0209	20.90	0.0632	63.20	52.67	47.33	0.0006	0.60
	82.98	2.00	2.00	0.0322	16.10	0.0238	11.90	0.1380	69.00	69.00	31.00	0.0060	3.00
	92.07	3.00	2.40	0.0571	19.03	0.0306	10.20	0.1992	66.40	83.00	17.00	0.0131	4.37
Cinnamon	68.03	1.00	1.20	0.0136	13.60	0.0262	26.20	0.0491	49.10	40.92	59.08	0.0111	11.10
	67.34	2.00	2.40	0.0255	12.75	0.0524	26.20	0.1035	51.75	43.15	56.85	0.0186	9.30
	92.07	3.00	2.80	0.0737	24.57	0.0379	12.63	0.1749	58.30	62.48	37.52	0.0135	4.50
Clove	83.82	1.00	1.10	0.0162	16.20	0.0095	9.50	0.0670	67.00	60.91	39.09	0.0073	7.30
	82.98	2.00	2.00	0.0377	18.85	0.0057	2.85	0.1409	70.45	70.45	29.55	0.0157	7.85
	92.07	3.00	2.70	0.0699	23.30	0.0115	3.83	0.2075	69.17	76.85	23.15	0.0111	3.70
Lemon	82.13	3.00	3.40	0.0133	4.44	0.0020	0.67	0.2406	80.20	70.76	29.24	0.0441	14.69
	90.17	5.00	4.80	0.0253	5.06	0.0023	0.46	0.4434	88.68	92.38	7.62	0.0290	5.80
	88.28	7.00	5.60	0.0100	1.43	0.0011	0.16	0.6683	95.47	92.82	7.18	0.0206	2.94
Orange	82.98	2.00	2.00	0.0110	5.50	0.0021	1.05	0.1548	77.40	77.40	22.60	0.0321	16.05
	90.17	5.00	4.80	0.0453	9.06	0.0063	1.26	0.3995	79.90	83.23	16.77	0.0489	9.78
	88.28	7.00	5.60	0.1040	14.86	0.0047	0.67	0.5145	73.50	91.88	8.12	0.0768	10.97
Wintergreen	90.17	5.00	5.20	0.0030	0.60	0.0360	7.20	0.4439	88.78	85.36	14.64	0.0171	3.42
Nutmeg	83.82	1.00	0.80	0.0195	19.50	0.0102	10.20	0.0536	53.60	67.00	33.00	0.0167	16.70
	91.12	4.00	3.60	0.0479	11.98	0.0187	4.67	0.3204	80.10	89.00	11.00	0.0130	3.25

Note.—Two extracts of wintergreen, one of nutmeg and the three peppermint extracts made in the laboratory were exhausted before this investigation of Howard's method was begun.

In all of these methods the fact is apparently ignored that in every case the volume that was originally occupied by the essential oil in the aliquot portion taken for the specific gravity determination is replaced by the alcohol-water mixture, thus making the results for alcohol too high. In other words, a true aliquot portion of the sample after removal of the oil is never taken. The error is increased in direct proportion to the amount of alcohol in the extract. Winton and Ogden[2] recognize the latter fault in the Official method in their modification which is as follows:

[1] "Commercial Organic Analysis," 3rd Ed., Vol. I, p. 162.

[2] Bull. **107**, U. S. Dept. of Agr., Bureau of Chemistry, p. 160.

[1] *Jour. Soc. Chem. Ind.*, **22**, 232 (1903).

[2] Report Conn. Agr. Expt. Sta., 1901, Part II, p. 172.

Thirty grams of the sample are diluted with water to 200 cc., the mixture poured into a dry Erlenmeyer flask containing 3.5 grams of light carbonate of magnesia, then well shaken and filtered quickly through a large dry plaited filter. The alcohol is determined in 150 cc. of the filtrate, the per cent. by weight in the extract being calculated by the following formula:

$$x = \frac{100ab\,(200 - cd/86)}{150c}, \text{ in which}$$

x = per cent. of alcohol by weight in the extract.

a = weight of the distillate.

b = per cent. of alcohol by weight in the distillate.

c = weight of the extract.

d = per cent. of oil by weight in the extract.

T. H. Harvey[1] also realized the need of a modification of the method and proposed the following:

TABLE III. RESULTS OF THE DETERMINATION OF ALCOHOL IN FLAVORING EXTRACTS BY THE PRESENT OFFICIAL METHOD FOR LEMON EXTRACTS.

(Results expressed as per cent. by volume.)

Kind of extract.	Composition of extract. Oil	Alcohol.	Alcohol found.	Per cent. of total oil in distillate.
Almond	0.50	26 27	26.30	...
	1.00	26.14	25 36	98.20
	1.50	78.92	78.94	99.33
Cinnamon	1.00	68 03	68.32	66 72
	2.00	67.34	67.20	45.77
	3.00	92.07	92.40	43.60
Clove	1.00	83.82	84.36	63.72
	2.00	82.98	83.96	49.23
	3.00	92.07	92.04	43.06
Cassia	1.00	68.03	68.32	64.74
	2.00	82.98	82.44	43.89
	3 00	92.07	92.04	39.10
Lemon	3 00	82.13	83.20	6.55
	5.00	90.17	91.68	3.58
	7.00	88.28	91.68	1.55
Orange	2.00	82.98	83.96	4.26
	5.00	90.17	91.68	3.08
	7.00	88.28	91.68	4.35
Peppermint	1.50	83.40	83.20	...
	3.00	82.13	82.44	...
	5.00	90.17	90.56	...
Wintergreen	1.50	67.69	67.70	21.40
	3.00	66.66	67.52	12.00
	5.00	90.17	90.56	9.24
Nutmeg	1.00	83.82	83.56	27.08
	2.00	82.98	82.84	20.15
	4.00	91.12	92.04	6.16

The extract is diluted to not more than three times its original volume, the liquor distilled and the distillate treated with about 0.5 gram of previously washed and dried kaolin to remove the undissolved oil. The specific gravity of the distillate is determined, and from the corresponding alcohol found the per cent. of alcohol in the sample is calculated.

[1] *Chemist and Druggist*, **1904**, p. 178.

In attempting to apply these methods to extracts in general, the fact should not be overlooked that dilution and filtering with magnesia or kaolin fails in many instances to effect the complete removal of the oil. It has been found in the case of extracts prepared in the laboratory that after diluting from 50 cc. to 200 cc. and filtering through magnesia, a clear solution was obtained, but, particularly in the case of oils which are more readily soluble in dilute alcohol, the distillate is cloudy when the first 60 or 70 cc. have passed over. On cooling the distillate to 15.6° C. for the specific gravity determination, a small amount of oil separates from the milky liquid. In order to determine the amount of oil carried over in the distillation, an assay of essential oil was made in each of the distillates obtained in applying the Official method for lemon extract to the extracts prepared in the laboratory. The results are shown in Table III.

In an extract composed only of alcohol, essential oil and water, the problem of determining the alcohol content may not present any serious difficulties. In such a case the determination of the oil and the specific gravity would afford sufficient data for the exact calculation of the per cent. of alcohol, as in the following:

Let S represent the specific gravity of the extract at 15.6° C., O, the specific gravity of the oil, and p the per cent. of oil found. Then $100 - p$ will be the per cent. of the water-alcohol solution, the specific gravity of which, represented by P, is calculated as follows:

$$S = \frac{Op + P(100 - p)}{100}, \text{ whence } P = \frac{100S - Op}{100 - p}.$$

The value of E, the alcohol equivalent of P, is obtained by means of an alcohol table and gives the per cent. of alcohol in the alcohol-water solution. To find the per cent. of alcohol in the extract, it is necessary to apply the following formula:

Per cent. by volume of alcohol in the extract =

$$E\left(1 - \frac{p}{100}\right).$$

In extracts containing other substances such as glycerine and sugar, recourse may be had to distillation in order to obtain a mixture consisting only of alcohol, water and essential oil. Having made the distillate up to the volume of the sample

of extract taken, the per cent. of oil and the specific gravity are determined and the alcohol content of the original extract obtained according to the above formula. There may, however, be some hesitation in accepting a method which requires a distillation and a second determination of essential oil, since for ordinary purposes in routine work the per cent. of alcohol can safely be derived from the specific gravity of the extract, providing the character of the sample be ascertained by a qualitative examination of the solids. In all cases where the oil can be separated by means of the centrifuge the alcohol may be determined as follows:

The alcohol-water liquor, freed as completely as possible from essential oil, is made up to 150 cc. in the test bottle for light oils and the temperature noted. In case the liquor happens to measure beyond the 150 cc. mark, the exact volume is read off on the stem. The liquor is poured into a distilling flask, the residue washed into the flask with about 30 cc. of water, the mixture distilled into the test bottle to near 150 cc. and the distillate made up to the original volume at the temperature previously noted. After thorough mixing, the liquor is cooled to 15.6° C., the specific gravity determined and the alcohol equivalent found. The result multiplied by the factor obtained by dividing the exact volume of the distillate by 50 gives the per cent. of alcohol in the original extract.

The extracts prepared in the laboratory were finally subjected to alcohol determinations, by the Official provisional method, by the method based on the determination of the specific gravity of the extract, by the application of the formulae given above and by the method applicable after the centrifugal separation of the essential oil. The results are shown in Table IV.

TABLE IV. RESULTS OF THE DETERMINATION OF ALCOHOL BY VARIOUS METHODS.

(Results expressed as per cent by volume.)

Kind of extract.	Alcohol in the extract. Strength used for solution of the oil.	Alcohol in the extract. Per cent. by calculation.	Per cent. by provisional method.	Per cent. by specific gravity without distillation.	Per cent. by calculation from specific gravity by formulae.	Per cent. by centrifugal method.
Almond	26.40	26.27	26.30	25.67	25 91	...
	26.40	26.14	25.36	25.27	25.78	...
	80.12	78.92	78.94	79.00	78.88	...
Cinnamon	68.72	68.03	68.32	68.09	68.03	...
	68.72	67.34	67.20	67.61	67.45	...
	94.92	92.07	92.40	93.17	92.13	...
Clove	84.67	83.82	84.36	83.94	83.75	...
	84.67	82.98	83.96	83.25	82.91	...
	94.92	92.07	92.04	93.00	92.02	...
Cassia	68.72	68.03	68.32	68.05	67.99	...
	84.67	82.98	82.44	83.28	82.95	...
	94.92	92.07	92.04	98.86	91.85	...
Lemon	84.67	82.13	83.20	85.00	82.55	82.26
	94.92	90.17	91.68	94.66	90.47	89.69
	94.92	88.28	91.68	94.48	88.65	88.42
Orange	84.67	82.98	83.96	84.97	83.27	83.06
	94.92	90.17	91 68	94.61	90.21	90.11
	94.92	88.28	91.68	94.46	88.45	88.55
Peppermint	84.67	83.40	83.20	84.41	83.47	83.58
	84.67	82.13	82.44	84.18	82.23	82.20
	94.92	90.17	90.56	93.67	90.13	89.58
Nutmeg	84.67	83.82	83.56	84.60	83.89	83.85
	84.67	82.98	82.84	84.54	83.10	82.20
	94.92	91.12	92.04	94.15	91.12	91.29
Wintergreen	68.72	67.69	67.70	66.86	67.57	6[illegible]31
	68.72	66.66	67.52	65.29	66.80	[illegible].97
	94.92	90.17	90.56	89.52	89.93	[illegible].01

CHEMICAL LABORATORY,
MINNESOTA STATE DAIRY AND FOOD DEPARTMENT,
ST. PAUL, MINN.

THE DETERIORATION AND COMMERCIAL PRESERVATION OF FLESH FOODS. SECOND PAPER—THE STORAGE OF BEEF AT TEMPERATURES ABOVE THE FREEZING POINT.

BY W. D. RICHARDSON AND E. F. SCHERUBEL.

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In a previous paper[1] we developed certain methods of analysis adapted to the detection of degradation changes in proteins and applied them to the question of determining whether or not changes of a chemical nature occur in leaf beef stored for considerable periods of time in the frozen condition, or in what is commonly called "cold storage" beef. The average of a number of analyses of fresh beef compared with a similar average in the case of frozen beef showed results so nearly identical that the conclusion was reached that no changes of a chemical nature occur in lean beef at temperatures below —9° C. for a period of 554 days and probably for a longer time; that is, changes which can be detected by the methods employed. It should be stated that the samples of beef used in the previous experiments when properly stored for over two years gave no indications to the senses of smell and taste of deterioration.

It remains to be demonstrated that the methods employed in the previous investigation were suitable to the purpose in hand; that is, that they were capable of detecting changes of a chemical

[1] *J. Am. Chem. Soc.*, **30**, 1515-64.

or biochemical kind which might occur in flesh foods under the influence of water, salts, acids, and such agencies as enzymes and bacteria. The way to determine the suitability of the methods would be to store meats under conditions wherein obvious changes ensue and to make analyses of samples at intervals. The purpose of the present paper is first to show that the methods are capable of detecting deterioration and second to follow by means of them the changes which occur when beef is stored in ordinary cooler temperature; that is, a few degrees above the freezing point—say 2–4° C. These temperatures—just above the freezing point—are the ones used by the large packing establishments for storing fresh meats, for shipping them in refrigerator cars, and for curing salt meats. In the butcher-shop and the home where meats are kept in ice-cooled refrigerators there is an approximation to the same temperatures, but for the most part in such storage the temperatures are higher and consequently deterioration proceeds more rapidly.

A sharp distinction must be made between the temperatures now being considered and those which were discussed in the first paper on frozen meats (—9 to —12° C.), for although with progressive lowering of the temperature the conditions for bacterial multiplication and chemical activity become steadily less, still down to the freezing point of water and many degrees below, suitable forms of bacteria develop and multiply very well in suitable media, provided only that the media are liquid. It is the solid condition which limits bacterial growth absolutely. In solutions which, because of the concentration of salts or other substances not decidedly antiseptic in nature, do not freeze at 0° C., suitable bacteria are capable of development at as low a temperature as —20° C. and possibly lower. Yet in solid ice at 0° to —1° C. they have no power of growth, although in the same medium, liquid, at 0° to +1° C. they would grow readily. Thus in frozen meats below —9° C. bacteria do not develop and cannot penetrate from the surface, while they grow readily in liquids at this temperature or below. Not that the juice of meat is solid at —9° C., but the solution which remains liquid is too concentrated and viscous to permit bacterial multiplication; and further, this solution in frozen meats remains at segregated points (mostly within the contracted muscle fibres) which are isolated by solid barriers of ice.

There is no doubt that the bacterial flora which causes the deterioration of meat (for this is mainly a bacterial process) at temperatures near the freezing point differs more or less from that which produces similar changes at higher temperatures. This is a subject which has not yet been accorded the thoroughgoing investigation which it deserves (because of its great importance from the hygienic as well as the economic standpoint) but each year adds some data to that available. The demonstration of the general principle stated, namely that a characteristic bacterial flora excites the deterioration of meats at temperatures near the freezing point, particularly in large establishments whose storage rooms are maintained at fixed temperatures for years, is not difficult. But on the other hand the work of developing a technique for the proper cultivation and study of these forms (in the case of salt meats as well as fresh) has not yet been carried out.

A number of experiments to try out the methods of analysis discussed in the first paper have been made during the past four years. Of these a few will be selected for presentation here. Those in which the tannic-acid-salt method of Bigelow and Cook for determining proteose nitrogen were used, will not be reported since the results obtained are too irregular and inconsistent. In place of this method the zinc sulphate precipitation has been adopted in all cases, although this determination (of proteose nitrogen) has not proved to be so important as some of the others.

Turning to the experiments, Table I shows the analytical results obtained by applying the methods referred to above, to meat undergoing bacterial decomposition at room temperature in summer, under the following conditions: A quantity of the lean meat from beef knuckles was hashed and well mixed. 100-gram portions were then weighed into liter flasks and 250 cc. of distilled water and 1 cc. of a putrefying meat infusion added.

The flasks were loosely stoppered and allowed to stand for different lengths of time (1 to 26 days) whereupon the samples were extracted with water, the extract made up to 1000 cc. and the analyses conducted.

The total solids show no essential deviation from the normal in one day, but thereafter an increase is indicated up to a maximum at five days and afterwards a decline.

The ash figures are approximately constant

except at the last, when a slight rise is shown. This increase has been observed in other cases but the determination is so liable to error that we are in doubt whether to ascribe the increase to the error of method or to actual augmentation during the decomposition.

The total nitrogen figures increase consistently and steadily from 0 to 26 days, beginning with a minimum of 0.819 per cent. and ending with a maximum of 2.744 per cent.

With some variations and irregularities the coagulable nitrogen reaches a maximum of 0.631 per cent. at 5 days and then drops to a point (0.206 per cent.) which is nearly one-half the normal amount.

The albumose nitrogen figures starting at near the normal reach a maximum in 5 days of about 9 times the normal and then fall off to three times the normal.

simpler forms. The insoluble tissues at first apparently become soluble and coagulable; or the containing membranes become disintegrated and allow their soluble contents to pass into solution in water. The albumoses precipitated by zinc sulphate may rise somewhat but only transiently while the main tendency lies in the direction of the formation of simple soluble basic substances volatile with steam and consisting principally of ammonia.

A series of experiments, which are, however, not altogether satisfactory, were carried out on hashed lean meat from beef knuckles, mixed with various preservative substances and placed in closed Mason jars at a temperature of 2° to 4° C. Chronologically these experiments preceded that just described, but logically they follow it. The results are shown in Table II. With the exception of a few irregularities, the tendency of the sub-

Table I.

Putrefaction Test on Hashed Beef Knuckle

100 grams meat, 250 cc. distilled water and 1 cc. putrefying meat infusion, held at room temperature 21–33° C. All figures on basis of meat. For methods used, see *J. Am. Chem. Soc.*, **30**, 1527-30

Date.	Age, days.	Moisture, per cent.	Ash, per cent.	Fat, per cent.	Total N, per cent.	Amm. N (I), per cent.	Amm. N (II), per cent.
6/3/08	0 (analysis meat)	74.84	1.25	2.52	3.57	0.034	0.010

		Cold water extract.						
Date.	Age, days.	Solids, per cent.	Ash, per cent.	Total N, per cent.	Coag. N, per cent.	Alb. N, per cent.	Meat base N, per cent.	Acidity, per cent. lactic.
6/3/08	0	6.11	1.25	0.819	0.417	0.027	0.370	0.83
6/4/08	1	5.93	1.19	0.840	0.453	.....	.....	0.83
6/5/08	2	6.96	1.19	1.078	0.549	0.085	0.034	0.60
6/6/08	3	7.14	1.29	1.428	0.476	0.143	0.809	0.57
6/8/08	5	9.36	1.31	2.093	0.631	0.196	1.166	0.47
6/12/08	9	8.86	1.33	2.121	0.527	0.137	1.425	0.75
6/29/08	26	6.64	1.31	2.744	0.206	0.087	2.506	1.40

Ammoniacal N (Method I) in extract at 8 days, 1.135 per cent.; 26 days, 2.055 per cent. Alkalinity to litmus 5 days equivalent to 12 per cent. N/10 acid; 26 days, equivalent to 26 per cent. N/1 acid.

The meat base nitrogen like the total nitrogen shows a continuous steady rise from 0.370 per cent. in the fresh sample to 2.506 per cent. in the oldest.

The ammoniacal nitrogen also increases steadily so that at the end about three fourths the total nitrogen is in a form which can be distilled with water in the presence of a mild alkali, caught in acid and titrated.

The acidity figures, on account of the presence of weak bases and weak acids, do not afford much information. With an indicator sensitive to weak bases the extract at the last is strongly alkaline; with one sensitive to weak acids it is noticeably acid.

In general the application of the methods to the extract from putrefying meat shows a continuous transformation of the nitrogenous compounds into

stances added (salt, saltpeter and boric acid) to arrest decomposition is well shown. It might be thought that the differences between unpreserved and preserved samples would be greater, but it should be remembered that the greatest influence against the growth of microörganisms in the experiment was the low temperature of storage. Small quantities of preservative substances are not to be compared with low temperatures as effective means of preservation of meats. Combined with low temperatures, they are very effective.

The next series of analyses shown in Table III indicates the changes which occur in pieces of firm lean beef stored at 2°–4° C. for considerable periods of time. This is the ordinary temperature used in storing fresh meats (and in shipping them)

in large establishments. The carcasses of the animals immediately after slaughter are run into the chill rooms where the temperature is brought down as quickly as possible from about 38° C. to near the freezing point. In some chill rooms the open brine system is used and in others the closed system. In the former system the circulating brine, previously chilled in the refrigerating plant, is allowed to overflow a notched trough or perforated pipe and to drizzle down sheets of cloth in the rooms to collecting troughs on the floor. In the closed system the cold brine merely circulates through overhead pipes. In either case, but chiefly in the open system, there is a considerable desiccating action exerted by the cold brine on the meats. There is, since the meats are warmer than the brine—and also, in the open system, since the vapor pressure of the brine is much less than that of the moisture in the meat at the same temperature, a continuous distillation of water vapor from the surface of the meat to the cold brine or brine pipes. This has the effect of desiccating and hardening to a certain extent the surface of the meat and thus making it more resistant to bacterial invasion. This surface desiccation is analogous in its results to the effects of the dry hard coverings enclosing natural fruits and other products and serving to protect them from decay.

TABLE II.

Progress of decomposition in hashed beef knuckles with various preservative substances added. Storage 2-4° C. added.

		Determined by analysis								Cold water extract.							
Test No.	Age, days.	Salt, per cent.	Saltpeter, per cent.	Boric acid, per cent	Moisture, per cent	Ash, per cent.	Fat, per cent.	Total N, per cent.	Amm. N, per cent.	Solids, per cent.	Ash, per cent.	Total N, per cent.	Coag. N, per cent.	Alb. N, per cent.	Meat base N, per cent.	Acidity, per cent. lactic.	
1	14	..	..	.	75.57	1.30	2.30	3.34	0.049	5.82	1.03	0.782	0.378	0.053	0.362	0.83	..
1	30	..	..		75.14	1.33	2.35	3.30	0.060	5.96	1.10	0.800	0.320	0.077	0.430	0.74	..
1	51	..	..	.	74.00	1.29	2.33	3.31	0.066	6.28	1.06	0.841	0.327	0.019	0.430	0.79	..
1	92	..	.	..	76.29	1.39	2.20	3.28	0.078	6.47	1.05	0.952	0.341	0.096	0.523	0.84	..
1	400	..	..	..	75.74	1.30	2.25	3.31	0.235	7.90	1.08	1.104	0.396	0.086	0.673	0.86	..
2	14	..	.	0.20	74.82	.	.	3.36	0.036	5.74	1.09	0.759	0.358	0.036	0.372	0.81	..
2	30	..	..	0.20	75.06	1.48	2.31	3.42	0.038	5.87	1.00	0.779	0.361	0.067	0.378	0.82	..
2	51	..	..	0.20	74.12	1.45	2.37	3.32	0.061	6.35	1.18	0.841	0.345	0.085	0.418	0.86	..
2	94	..	..	0.20	74.75	1.37	2.43	3.50	0.062	6.23	1.07	0.893	0.358	0.089	0.459	0.74	..
2	400	..	..	0.20	75.53	1.57	2.25	3.46	0.194	7.33	1.10	1.131	0.392	0.101	0.581	1.07	..
3	14	4.70	..	.	71.53	6.01	2.00	3.26	0.028	10.38	5.45	0.759	0.355	0.054	0.352	0.74	..
3	30	4.70	..	..	71.74	5.87	1.93	3.12	0.057	10.60	5.49	0.786	0.348	0.075	0.358	0.79	..
3	60	4.70	..		70.14	5.81	2.17	3.20	0.050	10.79	5.62	0.855	0.334	0.097	0.414	0.77	..
3	97	4.70	..	.	69.86	6.08	2.03	3.20	0.063	10.58	5.63	0.859	0.310	0.106	0.456	0.69	..
3	405	4.70	..	..	71.29	5.95	2.01	3.26	0.174	12.79	5.76	1.219	0.438	0.106	0.722	0.77	..
																	KNO_2
4	14	4.80	0.21	.	71.01	6.18	2.14	3.17	0.034	10.29	5.51	0.779	0.366	0.055	0.362	0.71	0.00
4	30	4.80	0.20		71.36	6.18	2.00	3.19	0.051	10.71	5.61	..	0.333	0.081	0.400	0.74	0.00
4	60	4.80	0.20	.	71.25	6.24	2.12	3.16	0.050	10.84	5.74	0.835	0.300	0.102	0.466	0.72	0.0035
4	99	4.80	0.17	.	71.33	6.05	2.14	3.14	0.059	10.76	5.62	0.897	0.284	0.168	0.463	0.61	0.0035
4	146	4.80	0.15	.	72.32	6.18	2.12	3.09	0.083	10.80	5.63	0.924	0.264	0.142	0.485	0.81	0.0026
4	405	4.80	0.003		74.30	6.18	2.10	3.14	0.193	11.82	5.93	1.310	0.456	0.124	0.720	0.48	trace
5	14	4.80	0.44		70.60	6.22	2.00	3.19	0.029	10.82	5.87	0.762	0.354	0.050	0.367	0.74	0.0012
5	30	4.80	0.44		70.04	6.24	1.98	3.06	0.050	10.65	5.60	0.755	0.313	0.091	0.400	0.73	0.00
5	69	4.80	0.39		71.67	6.21	2.21	3.16	0.053	10.95	5.90	0.828	0.280	0.133	0.399	0.61	0.0025
5	105	4.80	0.36	.	72.06	6.31	2.14	3.15	0.062	11.28	5.87	0.876	0.278	0.117	0.504	0.65	0.0026
5	181	4.80	0.37	.	72.34	6.18	1.91	3.19	0.099	11.61	5.90	0.913	0.256	0.093	0.560	0.75	0.0036
5	410	4.80	0.26	.	71.56	6.23	2.00	3.19	0.120	12.45	6.21	1.035	0.238	0.147	0.651	0.78	present
6	14	4.72	0.23	0.20	70.31	6.30	2.00	3.25	0.030	10.11	5.52	0.741	0.319	0.044	0.348	0.70	0.00
6	30	4.72	0.21	0.20	70.80	6.34	1.98	3.23	0.037	10.63	5.72	0.779	0.321	0.094	0.369	0.79	0.00
6	69	4.72	0.20	0.20	71.37	6.40	2.13	3.15	0.051	10.65	5.65	0.831	0.303	0.107	0.411	0.61	0.0055
6	111	4.72	0.19	0.20	71.92	6.34	1.91	3.13	0.053	10.66	5.56	0.869	0.289	0.105	0.474	0.74	0.0007
6	184	4.72	0.16	0.20	71.13	6.30	2.05	3.18	0.073	10.58	5.86	0.840	0.299	0.126	...	0.68	0.0009
6	410	4.72	0.13	0.20	71.90	6.32	2.05	3.17	0.107	11.18	5.92	1.004	0.250	0.136	0.615	0.83	present
7	14	.	.	0.45	74.82	1.70	2.24	3.43	0.040	6.12	1.38	0.765	0.357	0.054	0.352	0.81	0.0013
7	30	.		0.45	75.54	1.65	2.25	3.30	0.052	6.38	1.47	0.772	0.294	0.090	0.373	0.81	none
7	69	..	.	0.41	74.27	1.64	2.23	3.40	0.068	6.61	1.45	0.845	0.313	0.102	0.425	0.56	0.0055
7	110	..	..	0.40	75.27	1.59	2.23	3.33	0.073	7.51	1.46	0.931	0.307	0.090	0.544	0.78	trace
7	183	.	.	0.33	76.18	1.55	2.13	3.31	0.091	7.40	1.42	0.930	0.302	0.104	0.524	0.63	0.0052
7	410	..	..	0.20	75.52	1.64	2.10	3.34	0.123	7.68	1.41	1.053	0.281	0.121	0.622	0.76	present

It is true that even after the surfaces of meats have become more or less dry in the chill room as described above, if the air becomes saturated with moisture or nearly so, the meat surface will again absorb moisture, swell and soften and a

"slime" consisting of bacteria will develop and in time form a fairly thick layer on the surface of the meat. In a well ventilated, dry chill room this will not occur, even after decomposition has commenced.

Starting with recently slaughtered meat free from bacteria there are two ways by which micro-örganisms enter the flesh and excite decomposition: first, by direct extension of surface colonies into the firm tissue; second, by extension and locomotion along surfaces such as those afforded by blood and lymph vessels, and nerve and connective tissue sheaths.

By the first method, penetration is slow and very regular. The progress of the extension of the innumerable bacteria from the surface toward the interior can be easily observed. If a section be cut across a lean piece of beef which has been stored in the cooler for about 20 days or more, a dark narrow sharply defined border can be seen extending all around the cut. The line separating this border from the interior marks the limit of bacterial penetration by the first method. It will readily be seen that motility can not play a great part in this process; rather the advance occurs by the actual extension of the limits of those confluent colonies which have spread over the surface and later penetrated the meat. It will also be evident that the harder and drier the surface the less readily will penetration occur at the start, although after the surface layer is pierced progress will be easier. Hence the ad-

Table III.

Progress of decomposition in beef at 2° to 4° C Beef knuckles held at 2° to 4° C. and analyzed from time to time. Killed 3/2/08, cut 3/5/08. All figures on basis of meat. For methods used see *J. Am. Chem. Soc.*, **30**, 1527-30.

									Cold water extract.							
Lab. No	Rec'd.	Age, days.	Moisture, per cent.	Ash, per cent.	Fat, per cent.	Total N, per cent	Amm. N, Method I, per cent.	Amm N, Method II, per cent	Total solids, per cent.	Ash, per cent	Total N, per cent.	Coag. N, per cent	Alb. N, per cent	Meat base N, per cent	Acidity, per cent. lactic.	Remarks.
Av. anal. thirteen fresh beef knuckles			76.35	1.23	1.43	3.49	0.029	0.010	6.01	1.14	0.806	0.413	0.024	0.355	0.68	Average of 13 samples
2326	3/9/08	7	77.04	1.28	1.06	3.43	0.029	0.010	5.94	1.25	0.840	0.423	0.019	0.378	0.65	Meat sweet, venous color
2545	3/16/08	14	76.47	1.25	1.14	3.71	0.031	0.015	6.32	1.14	0.931	0.494	0.025	0.406	0.74	Ditto, surface slightly slimy
2761	3/23/08	21	76.87	1.20	1.44	3.62	0.030	0.015	5.67	1.14	0.791	0.362	0.028	0.378	0.77	Exterior shows distinct layer. Interior dull, turning purplish
2762	3/23/08	21	77.55	1.18	1.45	3.55	0.029	0.015	5.68	1.10	0.763	0.368	0.020	0.364	0.72	Sliminess increasing; odor of interior not bad
3182	4/2/08	31	77.46	1.15	1.94	3.42	0.065	0.017	5.59	0.93	0.805	0.381	0.038	0.374	0.61	Exterior layer increasing (10 mm.). Interior color dull as above. Odor interior not bad
3415	4/10/08	39	78.15	1.18	0.90	3.34	0.049	0.025	6.12	1.14	0.854	0.463	0.034	0.350	0.60	Exterior layer 15 mm. thick. Interior color brighter red.
Same, putrefying exterior portion							0.100	0.047								
3653	4/17/08	46	76.99	1.17	1.19	3.48	0.059	0.031	5.86	1.04	0.847	0.427	0.036	0.405	0.59	Very slimy and beginning to mould. Interior bright red. Bacteria localized throughout
Same, putrefying exterior portion							0.108	0.051								
3877	4/24/08	53	77.27	1.11	1.47	3.45	0.061	0.034	6.00	1.09	0.886	0.431	0.039	0.407	0.83	Ditto, but bacteria generally present throughout
4310	5/6/08	65	78.30	1.18	0.60	3.44	0.096	0.033	7.31	1.11	1.108	0.681	0.085	0.328	0.62	Ditto, Color duller but still red
5413	6/10/08	100	77.71	1.18	1.13	3.31	0.171	0.104	6.23	1.15	0.968	0.505	0.049	0.414	0.61	Ditto
8464	10/1/08	121	78.33	1.29	0.86	3.25	0.478	0.274	7.14	1.23	1.240	0.483	0.075	0.474	0.28	Ditto

Effect of freezing on putrefying beef: on 4/25/08 samples from the above lot were frozen and placed in closed tinned pails; later they were analyzed at intervals; for comparison the analysis of sample No. 3877 is repeated here.

3877	4/24/08	53	77.27	1.11	1.47	3.45	0.061	0.034	6.00	1.09	0.886	0.431	0.039	0.407	0.83
7101	8/12/08	132	77.30	1.19	1.38	3.41	0.071	0.036	6.69	1.14	0.987	0.488	0.042	0.474	0.47
9107	10/22/08	203	77.31	1.15	1.87	3.37	0.098	0.039	5.96	1.01	0.883	0.470	0.036	0.378	0.52
9108	10/22/08	203	77.79	1.19	1.09	3.35	0.094	0.032	7.33[1]	1.03	1.123[1]	0.728[1]	0.054	0.327	0.43
10538	12/3/08	245	78.91	1.12	1.30	3.20	0.091	0.041	6.64	1.00	0.974	0.506	0.055	0.413	0.39
10539	12/3/08	245	78.11	1.17	0.89	3.34	0.088	0.041	6.41	1.04	0.916	0.479	0.060	0.348	0.44

[1] For some unknown reason these figures appear to be abnormal.

vantage of a certain amount of desiccation in the cooler in the preservation of meats. Again the connective tissue which surrounds muscles and with which the ordinary large cuts of beef, mutton and pork are more or less covered is especially difficult of penetration by bacteria when it is dry. In this condition it resembles parchment.

The width of the bacterial border shown in section increases with the time of storage. Under favorable conditions at 2°–4° C. it will be about 1 cm. in 30 days; under unfavorable conditions (good desiccation) it may be only two or three millimeters in the same lengths of time. Fresh beef shipped abroad from Chicago reaches the ports of England three or four weeks after the death of the animal. It is needless to say that it arrives in a satisfactory condition of preservation.

It is characteristic of this method of bacterial penetration that the line of demarcation between the decomposing surface and undecomposed interior remains always sharp and distinct like the line marking the desiccation of the surface of frozen meats or soap.

The second method of penetration wherein bacteria follow various moist surfaces and tubes including arteries, veins, nerve sheaths, lymph vessels and connective tissue, allows them to reach at a relatively early period the interior of the meat, where they set up foci of decomposition which spread and finally merge with each other and the surface decomposition until the meat contains bacteria throughout and is in an active state of putrefaction. The extension of the interior foci can be roughly followed by making smear or impression preparation from various places on the surface of the sectioned meat, on cover glasses or slides. In the earlier stages of decomposition, infected and uninfected areas will be found side by side, the infected spots will be few and small, the untainted areas large. Gradually the former increase in number and size, the latter diminish until with the encroachment of the surface layer of bacteria no uncontaminated spot remains.

So far as the external surface is concerned if the air be dry no slime will form. If the air (and hence the surface of the meat) is moist a thick layer of slime will form and later an abundant growth of mould will appear. The slime consists of quantities of bacteria.

In the experiments about to be described the air was moist, thus preventing the formation of a dry surface layer and favoring decomposition and the development of slime and mould.

After what has been said it will be seen that the method of sampling of meat which is undergoing decomposition has an important influence on the analytical results. In general, the surface layer should be separated from the sharply differentiated interior, and analyzed separately. If slime or mould has formed on the surface, it should be washed, wiped or scraped off. In the early stages the decomposing surface layer is so thin that it is difficult of separation, but later the separation is easier.

In examining Table III it will be noticed that Laboratory No. 3182 was analyzed without separation of the surface layer—that it should have been separated is shown by the ammoniacal nitrogen being higher than that of the succeeding sample (No. 3415). In fact, it requires more than thirty-two days more of storage for the ammoniacal nitrogen figure determined on the interior portion, to surpass that shown in the table at thirty-one days. Later on there is no necessity for separating exterior and interior, inasmuch as the whole piece is in a condition of active decomposition.

It must not be supposed that in tests conducted upon a number of pieces of meat, which are undergoing decomposition, that the course of the process will be the same in each piece and that on a given date two separate pieces will yield the same analytical figures. Even though the pieces are as nearly uniform as selection will make them, there are still individual differences, of structure and of composition (differences of fat content for instance) which will modify the rate of penetration and multiplication of bacteria. It may even happen that similar pieces of meat exposed to apparently similar condition will yet be invaded by bacteria, the predominating races of which are different. Slight differences in the nutrient substratum will sometimes determine the preponderating variety. And so not only the relative abundance of bacteria, but also the relative abundance of different kinds with different chemical activities affects the course of chemical change in the decomposing material. Within limits, then the putrefaction of meat may assume very different aspects. The reaction may be acid or alkaline to litmus or other indicators, although it usually becomes alkaline to litmus and remains throughout acid to phenolphthalein. A great variety of acid and basic bodies may be produced under various conditions, aerobic and

anaerobic, and at various temperatures. Under anaerobic conditions we speak of putrefaction, under aerobic conditions of decay. Recent work indicates that characteristic stinking putrefaction can be excited only by anaerobes. In spite of the different courses followed in different cases of putrefaction its characteristics are sufficiently well defined to distinguish it from all other chemical processes. The same may be said of decay.

The meat used in the present experiments was the part known as the "knuckle" from the hind quarter of cattle. The piece is of very uniform lean composition, weighs usually seven to eight pounds and is somewhat conical in shape, seven inches in diameter at the base by fourteen inches high.

In one series of experiments, the results of which are shown in Table III, the knuckles were hung in a temperature of 2°–4° C. immediately after slaughter and were allowed to remain there during the period when analyses were made, that is for 121 days. When the knuckles had been in storage 54 days several were removed from the place of storage, frozen and held at —9° to 12° C. for some time longer. This was done in order to determine whether freezing arrests decomposition promptly or whether once started it continues in the frozen state.

In the other series of experiments (Table IV) knuckles which had been held in the frozen condition for 33 days were removed to storage of 2°–4° C. and held there for 120 days.

Moisture.—The moisture determinations are fairly constant throughout and require no special comment.

Ash, Fat, Total Nitrogen.—The variations which occur in these determinations are only such as might be expected in meat from different animals. They are not especially significant.

Ammoniacal Nitrogen.—The ammoniacal nitrogen determined by Method I remains nearly constant for 21 days in the case of the unfrozen samples and for 8 days in the case of the frozen ones. Had the exterior been separated, the ammoniacal nitrogen determined by Method I in the interior would undoubtedly have remained constant for a much longer time but this was not done until the samples were 39 and 23 days in storage, respectively, on account of the thinness of the bacterial border and the difficulty of its exact separation. The ammoniacal nitrogen determined by Method II remains constant for 7 and 8 days, respectively. As the meat ages there is a fairly regular and consistent increase in the amount of ammoniacal nitrogen by both methods. The apparent exceptions to the regular increase are

TABLE IV.

Progress of decomposition in beef which had been frozen for 33 days and was then transferred to a temperature of 2° to 4° C. Beef knuckles used in the experiment. All figures on basis of meat. For methods see *J. Am Chem. Soc.*, **30**, 1527-30.

										Cold water extract.							
Lab No.	Rec'd	Age, days.	Days in 2°-4°C temp.	Moisture, per cent.	Ash, per cent.	Fat, per cent.	Total N, per cent.	Amm. N, Method I, per cent.	Amm. N, Method II, per cent.	Total solids.	Ash.	Total N, per cent.	Coag N, per cent.	Alb. N, per cent.	Meat base N, per cent.	Acidity, per cent. lactic.	Remarks.
Average analysis thirteen beef knuckles				76.35	1.23	1.43	3.49	0.029	0.010	6.01	1.14	0.806	0.413	0.024	0.355	0.68	
2546	3/16/08	33	0	76.86	1 20	1.17	3.31	0.026	0 009	5.56	1.16	0.766	0.373	0.023	0.359	0.72	
2810	3/24/08	41	8	75.67	1.28	1.10	3.63	0.030	0.010	6.02	1.15	0.805	0.398	0.028	0.372	0.72	
3061	3/31/08	48	15	76.05	1.21	1 50	3.51	0.042	0.014	6.86	1.07	0 907	0.449	0 043	0.392	0 59	
3363	4/8/08	56	23	74.91	1 14	2.00	3.79	0.048	0 024	5.98	1.06	0.861	0.408	0.047	0.388	0.73	Bacteria at isolated points in interior
Same, putrefying exterior portion								0.092	0.040								
3369	4/9/08	57	24	76 42	1.15	1 41	3 55	0 051	0 024	6 11	1.08	0.872	0.449	0.049	0.353	0.72	Bacteria at isolated points in interior
Same, putrefying exterior portion								0 111	0.047								
3635	4/16/08	64	31	76.14	1 16	1 55	3 53	0 049	0 029	5.83	1.10	0.819	0.426	0.041	0.372	0.61	Bacteria at isolated points in interior
Same, putrefying exterior portion								0.122	0.046								
3878	4/24/08	72	39	76 18	1 30	2.01	3 63	0.058	0 032	6.60	1.11	0.931	0.516	0 041	0 380	0.73	Bacteria generally distributed throughout
Same, putrefying exterior portion								0.106	0.051								
4311	5/6/08	84	51	77 34	1 17	1 11	3 48	0 092	0 039	6 18	1.04	0.917	0 504	0 074	0.329	0.57	No distinction between exterior and interior
5456	6/11/08	120	87	76.70	1 24	1.89	3.56	0 198	0.120	6.97	1.18	1.074	0.534	0 056	0.467	0.39	No distinction between exterior and interior

to be explained as before stated, by the inclusion of the bacterial surface border with the undecomposed interior. It appears that the ammoniacal nitrogen, determined by any one of several methods, increases regularly with bacterial decomposition. Yet it cannot be said positively that it is characteristic of bacterial hydrolysis only, since the ammoniacal nitrogen increases to some extent in acid and alkali hydrolysis and peptic and pancreatic digestion of proteins. The relationship between the ammoniacal nitrogen produced by the agents mentioned requires further study. In the absence of the other hydrolytic agents, the production of ammoniacal nitrogen can be definitely ascribed to bacteria.

Total Solids in Cold Water Extract.—On the whole the total solids in the cold water extract appear to increase with the age of the meat and hence with the increase of decomposition. This increase is not marked except in the oldest samples, and even then does not reach a very high figure.

Ash in Cold Water Extract.—The figures as would be expected are nearly constant throughout.

Total Nitrogen in Cold Water Extract.—There is a fairly regular increase in the nitrogen in the cold water extract from the beginning to the end of both experiments. The increase is altogether greater (as in other experiments also) than the increase in total solids.

Coagulable Nitrogen in Cold Water Extract.—The coagulable nitrogen shows, on the whole, a tendency to increase, although this is not regular and never reaches a larger amount. It is most marked in the oldest samples.

Albumose Nitrogen in the Cold Water Extract.—The albumose nitrogen determined by the zinc sulphate method increases, although somewhat irregularly, with the age of the samples. The total amount is never large and this would indicate that the albumoses are rather quickly transformed into simpler substances—those we have grouped under the term "meat bases."

"Meat Base" Nitrogen.—The "meat-base" nitrogen gradually increases with increasing age and decomposition.

Acidity.—It is doubtful whether in a product like meat, the lean of which is composed almost entirely of proteins, any fermentation could result in decidedly altering the reaction provided the indicator used is sensitive to weak acids as well as to ammonia. The fermentations of carbohydrates and fats produce acids, but these compounds contain no nitrogen or basic groups.

While there are some contradictory figures in the analyses of the samples which were frozen after being stored at 2–4° C., from the results the conclusion may fairly be drawn that freezing of meats at —9° to —12° C. arrests bacterial decomposition but can not in any degree restore the product to its original condition.

ADDRESSES.

THE EFFICIENCY AND DEFICIENCIES OF THE COLLEGE-TRAINED CHEMIST, WHEN TESTED IN THE TECHNICAL FIELD.[1]

By William H. Nichols.

The subject which has been assigned to me as part of this symposium is one which I would hardly have dared to bring forward of my own motion. It must involve us occasionally in statements which are not complimentary to either student or professor, but which are nevertheless true. Of course there is much that is of a more agreeable character, and this is naturally the more attractive side; but if it were the whole question, we would have reached perfection, and instead of a discussion we might satisfy ourselves with a summing up of our accomplishments, ending with a genial benediction, and go away with a snug feeling of thankfulness that we were not as other men. I cannot, however, forget my own experience while a student of chemistry and its applications, and the painful failures which ensued while subsequently endeavoring to put my learning into practice; and it is conceivable that these recollections may have had an undue influence on the result of my observations of others for a period of nearly forty years ensuing, during which time I have come in familiar contact with many college-bred chemists. The gradual though steady improvement in processes and methods to be noted, indicates the constant tendency to greater efficiency, while the comparative slowness of this improvement is doubtless partly due to some of the deficiencies in the preparation for the work. When I compare the attainments of recent graduates with my own when I went out into the world in 1870, I readily notice how much farther along the college work has brought them, and how much better prepared even the dullest or laziest of them is, than any of the students of my day. This applies to analytical and research work, as well as to chemical engineering, which then was extremely rudimentary and commonplace, usually given over to men who had been brought up in the works and without any scientific training.

The college course, of necessity, must be more or less general. With a hundred or more students of varying attainments and ability, it is impracticable to treat them as units, although I am aware that frequently all that is possible is done in this direction, particularly in the upper classes. From the technical point of view, there are three great fields in chemistry, and the student should himself decide which of these he intends to occupy. If he does not

[1] Read at Baltimore meeting, American Chemical Society, December 29, 1908.

do this of his own accord, his instructor should, I think, do it for him, after he has become acquainted with the student's measure. If during the ordinary course, the student or professor has not been able to make this selection, a post-graduate year should follow, always provided that the student's work shows that he has not been mistaken in selecting chemistry as a profession. In many cases it would be a kindness to suggest the taking up of some less exacting science, and some of the deficiencies are doubtless due to this effort to make synthetically a chemist out of impossible elements.

The three fields alluded to are those of analysis, research and technology or engineering. The first is of course essential to both of the others, and yet it is a pursuit by itself, and many follow it all their lives, either in works laboratories or as public analysts. As a rule, in this department, originality is not essential, the work being one of detail constantly repeated. Naturally, there are exceptions, and many of the best analytical processes have been worked out by men of this class. While this is not the highest branch of the science, it is at least the foundation, or more properly speaking, the root. There is no reason why any college should be deficient here, as it is only a question of professor and laboratory. Of course the institution cannot be held responsible for the student's inability or unwillingness to absorb what is generally so well given, although it may be criticized for not weeding out the stupid or lazy, and thus make needed room for others who hold out more promise. But certainly, it must be the fault of the college or professor, if a man be allowed to graduate who is not a good analyst, fitted to go on with routine work even while admitting that some institutions give a far better preparation than others. The science is open to all, but some men have a much better ability than others to impart knowledge that will be comprehended and absorbed.

The second of the fields alluded to as being open to the chemical student, while embracing the first, is of far greater importance and extent. I allude to the field of research. If during the college course, the student has not received some inspiration in this direction, there is a "screw loose," somewhere. If it be approximately true that if a man finishing the chemical course be not a good analyst, it is probably his own fault; it is, I fear, equally true that if he be not imbued with a determination to put his knowledge to uses that will produce new results, it is because his instructor has not been a man filled with an enthusiasm which he must communicate. A teacher of chemistry who imparts the dry facts of the science without holding out alluring glimpses of its future possibilities, is robbing his charges of their rights, for chemistry is the great science of the future, on which the welfare of the world, if not the very lives of its inhabitants, will depend more than on any other. But it must not be forgotten that research in chemistry must be conducted on common sense principles, and these include fixed purposes and objectives. Research on general principles is apt to produce general haziness and absolute lack of concrete useful results. But here we must make two subdivisions, lest we lose sight of the value of the magnificent work done in abstract research. It is very easy for us to understand the value of research which immediately results in the production of a new article, or an improved method of making an old one; but it is not so easy to appreciate the bearing of an abstract research which simply adds certain knowledge to our store, or opens to us some new law, which in our present state of ignorance has no bearing that we can discern, but the knowledge of which will be essential to some great discovery of the future, which in its turn will lead to others and still others *ad infinitum*. The purpose of this paper is not to discuss the importance of chemical research, which is one of the most attractive subjects I can imagine. Hence, I must not dwell too long upon it. I think I have said enough, however, to remind us of the responsibility under which instructors labor in this regard. The man who for four or five years each has a number of receptive minds looking to him for light, falls far short of his duty and opportunity if among those minds he has not stirred up, according to the measure, an intense desire for working into the future. The field of chemical research, both abstract and concrete, being one of the most important that the human mind can engage in, it is gratifying to feel, as I do, that there has been a steady improvement in this regard, in the training of men fresh from college, which indicates that instructors in many cases are fully alive to the importance of the subject, even if they appreciate that much remains to be done.

The third field alluded to for the chemical student, is that including applied chemistry, so called, and chemical engineering. The former of these two subdivisions covers a much larger territory than the latter. While thirty years ago, the use of a chemist in the ordinary manufacturing establishment was the exception, it is at present, I am happy to say, the rule. This is now so well known, and the reasons or rather necessities for it are so well understood, that nothing more than the allusion is needed. There is no reason, so far as I can see, why college and technical schools are not pretty well equipped to furnish men trained to be of great service in this field, not only for the careful watching and control of the work, but for research in the special lines looking to improvements and economies. Almost all kinds of manufacturing establishments are open to the teaching staff and students alike, and the best practice employed in nearly all industries is well understood within the college walls. Details of cost and production are generally ascertainable, and the professor's lectures may be kept fairly well up to date. Therefore, there is little reason why the graduate chemist who has had this line of work in mind, should not soon become useful, and thereafter steadily improve. In addition to his knowledge of chemistry, the more he knows of engineering the better, particularly if it be of a nature to enable him to apply his chemical knowledge to the needs of the particular establishment. The general manufacturer need have no hesitation in adding to his staff, graduates in applied chemistry of many of our institutions.

With chemical engineering, the case is somewhat different. As I said at the beginning, thirty-five or forty years ago, work coming under this head, was in this country performed almost exclusively by practical men brought up in the works, whose deductions were the result of experience unenlightened by theory. It was, of necessity, somewhat crude, but good enough for practical purposes while every chemical manufacturer was in the same boat. The advent of the college-trained man changed all this, and the uneducated engineer has been gradually relegated to the background and for obvious reasons. The advantage the college-trained man had

was in his knowledge of the theory of chemistry. His disadvantage frequently, was his utter lack of engineering knowledge to enable him to apply it practically. The theory was of more value than the rough engineering without it, for engineering ability of high order has long been obtainable, and thus, theory could have a respectable application. There have been brilliant cases where both existed in the same individual, but I am compelled to say, that as far as my observation goes, this has not been general or even common. Now it must not be forgotten that the converse of this proposition may be true, though I do not think equally so. If the chemist may look to the engineer for assistance, why may not the relation be reversed? My answer to that is that it may be and generally is, in manufacturing establishments of a general character. In the chemical works, however, where the highest application of the theory is aimed at, chemistry should be the guide, and engineering the servant. If the chemist can also be the engineer, so much the better, and so much more likely will he be to bring his theory to fruition. And just here is where a great difficulty presents itself. The theory of chemistry is open to any who desire it, and who have the capacity to absorb it. This is hardly true of its application in the manufacture of chemicals. The student of Electrical Engineering has not only the theory at his command, but his text books have the latest practice, and he may visit the newest plants, and study them to his heart's content. So also with the student in Civil, Mining or Mechanical Engineering. These may in addition have their Summer Schools and field work, with the opportunity thus afforded for actual work under the most favorable conditions. In addition, the instructors are frequently employed in consulting capacity, and are thus up to date in many of the finer details of what has been accomplished, and what is being considered for future accomplishment.

It is not so with the student of Chemical Engineering. His text books contain, frequently, old processes and sketches of antiquated plants, or details accessible only after the process itself has been discarded or the plant abandoned for something better. His instructor is frequently in no better situation; and his lectures are sometimes, I fear, records of what used to be. I do not see how this sate of affairs can be greatly changed, until chemical manufacturers open their works to both professor and student, a course which the exigencies of competition would seem to be likely to postpone indefinitely.

What, then, shall we teach our students who are preparing for this field? First of all—chemistry, all they can absorb. After this, as much Electrical and Mechanical engineering as possible, for both branches have come far to the front in modern chemical works. The chemical manufacturer who takes the graduate into his works will thus be able to make his instruction partake more of the nature of postgraduate work than is now so frequently the case.

A discussion of this question would fall far short of completeness if we did not take into consideration other matters than simply chemistry and engineering. The whole question of education in general has merited and received an immense amount of attention, particularly during recent years. While naturally, there have been many views, differing in detail, and sometimes widely divergent, it is, I think generally admitted as the consensus of opinion, that the object of education is to make the most that is possible out of the material in hand, on the lines for which the student is more especially adapted. This education received at college or elsewhere, is the foundation upon which the real education of the student is to be based; which real education can only be acquired in after life, as the result of study, experience and association with others. The college has done its work when it has provided the student with the best possible foundation, and naturally his future depends to a large extent upon himself.

This preliminary education, if it may be so termed, would lack what the student has a right to expect, if it ceases when it has made him a good chemist with ambition for research and even with a good knowledge of engineering, which have been cited in what precedes, as the three necessities of the college curriculum for the production of chemists.

There is no reason, after all, why a chemist should not be qualified to assume the general duties of citizenship as well as the members of any other profession; and therefore, during his college course he must have something more than pure science. No man can fulfil the possibilities of his life if he be altogether one-sided or lop-sided; the educator should endeavor, so far as possible, to round out all of the faculties of the man. To do this, culture studies must not be omitted; particularly such culture studies as would tend to elevate the literary, the artistic or even the imaginative side of the student.

In preparing a man for life in the chemical field, he should be filled with the idea that any position in that field is open to him if he have capacity, industry and honesty, and he should look for attaining no position that is lower than the highest. This he cannot hope to do unless by the absorption of culture studies, he has prepared his aesthetic side as well as his scientific, although, perhaps, not to so great an extent.

I am well aware of the limitations imposed upon by the necessarily short time the student has in college—usually four years, rarely more than five—in which to acquire all that a man needs in the scientific line to become useful in his chosen profession of chemistry. I am aware that a good deal of work will have to be added if he is to have the engineering knowledge which I have alluded to, and have his mind cultivated by literature and kindred branches; and I imagine that the criticism will be made that it is impossible for any man to do the amount of work necessary to accomplish this result. It seems to me that the answer to this is, that with the modern idea that education is only begun in college, there is no reason why such tendencies should not be produced in the mind of the student, so that all of the necessaries of a rounded education should follow by his own later work. It is only necessary to allude to that honored man who has recently announced his intention of retiring from the presidency of Harvard University, and who, although a chemist, rose to a position of great power in other fields, as instanced by his latest office; or to that other college president, who, while a great chemist, has presided with such dignity and force over the University which has been such an honor to this City of Baltimore. There are many other instances which will occur to you, but these two will suffice to show the possibilities to which men educated as chemists have a right to expect to attain.

To sum up briefly what I have so imperfectly expressed;

there is no reason why any college should not turn out good analysts and research chemists. If the graduates fail in these particulars, it is largely due to inefficient work of the professor or the college itself. There is sufficient reason why colleges should fail in turning out good chemical engineers, and for this failure I do not think they should be held altogether accountable, provided they do what they can in the direction of furnishing engineering attainments to the chemists. I believe that nearly all colleges are more or less deficient in the culture work which is given to their chemical students, and I see no reason why this deficiency should continue. They have the means at their command and should insist upon the student availing himself of them.

But after all, the greatest deficiency will be found to reside in the student himself, who either wilfully or from lack of ability, does not take full advantage of the opportunities afforded. In this respect the chemical student is no exception to the general rule the world over, and I suppose that to the end of time, brains, carefully cultivated and backed by initiative, will be at a premium.

THE UNTILLED FIELD OF CHEMISTRY.

Address of the Chairman of the Division of Industrial Chemists and Chemical Engineers, Baltimore, December 29, 1908.

By Arthur D. Little.

Two years ago, upon a similar occasion, it was my privilege to address many of you and to point out some of the relationships existing between the chemist and the community. In so doing, there naturally devolved upon me the pleasant duty of recalling to your minds a few of the great and more significant achievements of members of our profession by way of indicating, although briefly and most inadequately, something of the extent to which the chemist has already placed the community in his debt. It is good for any body of men, animated by a common purpose, to take, from time to time, mental stock of what they have accomplished and of the relation in which they really stand to their environment. Whereas in our own case, the record is one of which we all may well be proud, its contemplation brings a new sense of the dignity of the work itself, a pride of fellowship and an incentive to increased endeavor.

We move, however, in a world where it is easy to take much for granted, where symbols and conventions quickly come to take the place of the realities they represent. Our mental processes are apt to run along the line of least resistance and the apparent and the obvious obscure the fundamental truths. This being so, we can well afford to leave our achievements in the security of the past while we consider for the moment the things we have left undone.

The volume of chemical literature has become so great, so many compounds have been described and classified, so many methods have been laid down, so much of detail confronts the student, and his field of study has been so subdivided as to suggest and foster the delusion that the total sum of chemical knowledge must be vast indeed. Vast in its detail perhaps it is, but lacking in those fundamental unities which out of the confusion of detail bring wisdom. Chemistry still awaits its Newton. It still justifies the estimate of Kant who said of it more than 100 years ago:

"Chemistry is a science, but not a science in the highest sense of that word; that is, a knowledge of nature reduced to mathematical mechanics."

Despite the immense amount of dry detail which we have accumulated and in some measure correlated, chemistry is still in the imaginative era where generalizations are more the result of happy inspiration than of close mathematical analysis.

Chemistry concerns itself with the changes which matter undergoes in its varying relations to certain forms of energy and yet we do not know what matter is nor have we any conception of the real nature of energy. One has only to state in their ultimate terms the problems confronting us to bring a realization of how very far from their solution we still stand. They are, for instance, thus summarized by Karl Pearson:

What is it that moves?
Why does it move?
How does it move?

Where, yet, I ask you is their answer to be found in chemistry?

We have built our science upon the assumption that matter, whatever that may be, is composed of indivisible atoms, of a comfortable and ultimate simplicity, only to find that the atom is in fact divisible and that its structure is undoubtedly complex beyond imagination. As to those phases of energy which are concerned with chemical change, even so great a philosophical chemist as Otwald says: "Chemical energy is to us the least known of all the various forms, as we can measure neither it nor any of its factors directly. The only means of obtaining information regarding it is to transform it into another species of energy."

So we have gone on for a hundred and fifty years transforming chemical energy into electrical energy or into heat, making minutely refined measurements of the relatively small amounts of energy appearing in our processes, while wholly unconscious all this time of the stupendous stores of potential energy which we now vaguely begin to realize are bound up in matter.

Our study of matter has led us to teach that it manifests itself in some seventy distinct and separate forms which we call elements, and yet our very definition of an element is a confession of our failure. An element is something which we have not been able to decompose into anything simpler. We have discovered some curious and interesting relationships between the elements which point to their common origin. In his heart each one of us believes that they must have had a common origin and that the cycles of development which they exhibit can have resulted only from the action of a periodic variable upon a constant and yet we very rarely even consider the question of their genesis or why their properties are what they are. We are content to regard them as so many distinct creations. The discovery of a new element is hailed as marking an epoch in the history of our science when our real business should be the elimination of the elements as such.

In their interactions, the elements, as we know them, manifest valences and selective affinities which determine the course of all chemical change and yet we are without an acceptable working hypothesis of the cause and nature of either valence or chemical affinity. Our ideas regarding the constitution of the molecules of many compounds have been developed in great detail and have led us to so many happy conclusions which the facts have verified as to justify our belief that these ideas must rest upon a substantial

basis of truth. This sometimes leads us to forget that the graphic formulas which we build up and write on a plane surface are an attempt to represent in terms of two dimensions actualities which exist in three. Moreover, these formulas depict the molecule as something fixed and rigid although everything tells us that the atoms within the molecule are in rapid and ceaseless motion. A new chemistry will dawn when we take proper cognizance of these motions and their influence upon the properties and relations of the compound. We state molecular weights with a finality of assurance, forgetting that we know very little of the molecular weights of liquids and nothing of the molecular weights of solids. We write cellulose as $(C_6H_{10}O_5)_n$ but the unknown n is probably the most significant part of the entire formula.

Sulphur passes before our eyes from the crystalline to the amorphous variety, phosphorus assumes the red or yellow form and an almost complete change of properties attends the transformation. Carbon exists in several markedly different states, and yet as to the meaning and mechanism of these molecular changes we remain in complete ignorance. Fortunately for the comfort or even the very fact of our existence upon the planet water is denser at 4° than it is at zero. Had it not been so, our lakes and oceans would be simply so many solid ice masses upon which the summer sun could make only a superficial impression, but, in spite of the paramount importance of the fact itself no one of us can say why the water molecule presents this curious anomaly. We write the water molecule as H_2O and commonly regard it as a relatively simple compound. How then shall we account for the fact that the dielectric constant or specific inductive capacity of water is about fifty times that of air, or perhaps ten times that of glass. As the dielectric constant is in a sense a direct measure of the massiveness of the molecule, are we not forced to the conclusion that the water molecule really is built up of many of these H_2O groups? How else indeed shall we explain the power of water to knock asunder the molecules of electrolytes which it dissolves and does not this complexity of the water molecule bear some relation to the essential part which water plays in the ultimate phenomena of living matter?

And this brings me to the main point of my thesis. A great German chemical company tells us in an attractive book just issued that it employs 218 chemists, 142 civil engineers, 918 officials, and nearly 8,000 workmen. It covers an area of 220 hectares, has 386 steam engines, 472 electric motors, and 411 telephone sub-stations. The plant represents the highest development which industrial chemistry has reached, but none the less it cannot produce an ounce of starch which a potato growing in the ground fabricates from water and carbonic acid gas under the influence of sunshine.

True it is that this great aggregation of engines and dynamos, furnaces, retorts, and stills can, under the direction of its highly trained and specialized chemical staff, produce certain natural products in condition so available and pure as to even improve upon nature, but by what monstrous effort is it accomplished? In the spring the tender grass and the delicate unfolding leaves cover the whole earth with the green of chlorophyll. There is no noise, no smoke, no stench. The grass is cool and grateful to the touch and clean. In similar manner vegetation everywhere is fabricating cellulose to the extent of several billion tons each year, and not only cellulose, but all the countless other complex products of the vegetable cell. What shall we say of our own chemistry in the face of facts like these, except that we have gone far enough to encourage a faint hope that we may some day be able to approach such methods. Professor Wheeler has defined so clearly a thought which has been in my own mind for years that I cannot do better than quote his words. He says:

"The vegetable cell is a laboratory in which are carried out a most remarkable series of chemical reactions. As we contemplate the immense number of organic compounds of all degrees of complexity which are formed within this wall of the plant cell we are convinced that this is the chemical laboratory *par excellence*. Two features impress us particularly: first the silence in which the operations are carried on; second, the narrow range of medium temperatures required. Notwithstanding this apparent simplicity of conditions, the products are of the most varied kind. Some of these men are able to synthesize in their own crude way; others are still the secrets of nature. It is utterly impossible for man to prepare certain naturally occurring compounds except at a temperature which would burn the plant tissue. We are led to wonder whether forces exist with which we are unacquainted or whether we are merely unable to control the forces already familiar to us. It would be difficult to say which supposition is the more probable. It will be granted that investigation into the activities of the cell is of profound importance. In fact, it has been said that "it is in the plant cell where synthetical operations are predominant, that we have to look for the foundation of the 'New Chemistry' which may be expressed broadly as the relation of matter to life."

I expressed two years ago my own belief that the distinctions which we now regard as fundamental between living matter and dead matter would soon break down. This break will in my opinion come through the study of the colloids which are the link between matter which we regard as living and that which we regard as dead. At this point, I cannot refrain from volunteering a suggestion. We know that the atoms within the molecule are in rotation. It must follow that as the complexity of the molecule increases, more and more of its motion of translation must be converted into rotary motion. In the colloidal molecule we know that many simpler molecules are linked together, and in the molecule of living matter, what? May it not be merely that the more or less haphazard and confined movements of the molecules which together build up the colloid are in the molecule of living matter coördinated and controlled in a manner which suggests the vortex? Dead matter drawn within this vortex would partake of this movement and exhibit the phenomena of life. Matter thrown off tangentially would resume its rectilinear course and become for the moment dead.

When we consider that in theory at least, in which accidents are barred, a tiny bit of living jelly, an amoeba for example can endow with life an ocean of its proper pabulum, it seems obvious that the forces which are to manifest themselves in the phenomena of life are already existent in the pabulum and that what the living jelly does is to induce a coördination and direction of the atomic movements which then take on the vital aspect. Do we not have something

roughly analogous to this in the magnetization of successive pieces of steel drawn across a lodestone? A certain coördination of movement in the molecules of the steel has been induced and magnetism results. So in some manner far more complex, life I believe may be epitomized as coördinated motion.

The subject-matter of such speculations lies so far outside our present-day chemistry as to almost require apology for their presentation, but they are well within the subject-matter of the chemistry of the future, for, to again quote the words of Pearson:

"The goal of science is clear, it is nothing short of the complete interpretation of the universe."

Or as Muir has put it:

"The great business of chemistry is to force men into close contact with some aspects of external realities and, with the help of her sister sciences, to remove everything that prevents the full vision of nature."

NOTES.

THE METHODS OF THE UNITED STATES STEEL CORPORATION FOR THE COMMERCIAL SAMPLING AND ANALYSIS OF IRON ORES.

IRON ORE SAMPLING IN GENERAL.

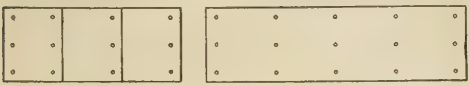
Owing to the varying conditions under which iron ores must be sampled, both by the producer and the consumer, variations from any uniform procedure of sampling are necessitated. The elements of time, size of shipment, kind of ore and other considerations are determining factors in the details of procuring the sample. Hence it is the purpose to render the following methods general in their scope, promulgating those ideas applicable in the broader sense to ore sampling, without attempting to prescribe for ever varying and unforeseen contingencies in the details.

CAR SAMPLING AT PRODUCER'S END.

All samples must be taken uniformly over the surface of the cars after being loaded by taking a minimum of twelve places for wooden, and fifteen places for steel cars, by either the parallel or the zigzag system. The following diagrams illustrate these two systems and show the minimum number of points where samples are to be taken.

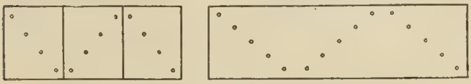
PARALLEL SYSTEM.

25 TON WOODEN CAR. 50 TON STEEL CAR.



ZIGZAG SYSTEM.

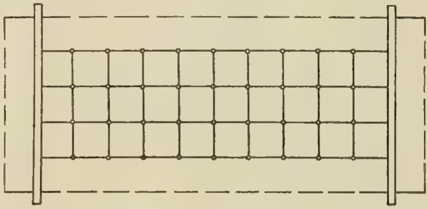
25 TON WOODEN CAR. 50 TON STEEL CAR.



When lumps of ore are encountered at the designated points where samples are to be taken, small portions of each lump must be chipped off, about equal in size to the first joint of the thumb. When rock occurs it must also be sampled as ore, that is, a proportionate amount of the rock or off grade material is to be taken, not equal in amount to the regular sample for the area covered by that point, unless the entire area is such off grade material. Then the same amount of adjacent material must be taken, ore or rock, equal in amount to the portion taken at each regular point. This also applies to field boulders, unless thrown from cars.

The samples are taken with a garden trowel. Each ten cars, either steel or wooden, must be combined, as a rule, into one sample; but less than ten cars may be grouped. The weight of the sample must not run under fifteen pounds for ten wooden, and twenty pounds for ten steel cars.

Whenever very lumpy ore is to be sampled in the cars, the rope net system is used as shown below, which gives about thirty-two places on each car, the knots being eighteen inches apart. In using the net system, if a lump of ore or rock comes directly under the knot, a piece should be taken about the size of the first joint of the thumb. If fine ore occurs under a knot, an equal amount is taken with the trowel. The rope net system is used at the Marquette Range on the hard, lump ore; also at the Soudan Mine, Vermilion Range.



A moisture sample must be taken for each train load from all open pit mines; a train consists of forty to forty-five of the fifty ton steel cars, or sixty to sixty-eight of the twenty-five ton wooden cars. A moisture sample must also be taken for all the cars loaded at a shaft or stockpile during each ten hour shift. Samples must be taken from three places on top of each car as shown by the following diagram.

Care should be taken to secure the sample from well underneath the surface as soon as practicable after loading, maintaining the true proportion of lump and fine ore. The sample as taken must be immediately placed in a can with a tightly fitting lid, and brought to the crusher house. It is optional to take a moisture sample from the regular sample, provided it has been taken from well underneath the surface.

CARGO SAMPLING AT CONSUMER'S END.

Cargo ores present the most serious obstacles to a uniform method of sampling. The boats vary in size from three thousand to twelve thousand tons with one or two decks, and in the number of hatches from six to thirty-six with widths varying from twelve to twenty-four feet. The

grabs at the different unloading points vary in number, kind, size, and the rapidity of their operation. The ores vary from the very fine to the all lump, from the so-called mixed ores such as the groups to the mixed cargoes, consisting of different ores in the same boat, and with different ways of loading the boats.

Grab Sampling.—An excellent method of cargo sampling where the entire cargo will be represented, and particularly adaptable for fine ores is called grab sampling. A sampler with a small scoop attached to a handle of suitable length and holding a definite amount of ore, a quarter, a half, or a whole pound, takes a scoopful from each grab as it rises above the deck. The disadvantage of this system is its increased cost due to the extra number of samplers, one being required for each grab during the entire time of unloading.

The general plan for the sampling of all cargoes is to first sample the tops of the piles, before the grabs have started to unload; this is called sampling of the cones. After the grab has removed from the hatch all the ore within reach, the exposed faces standing on each side are sampled; this method is known as face sampling. Or when the latter practice is impracticable owing to the operation of the grabs, then the method of rounds is followed.

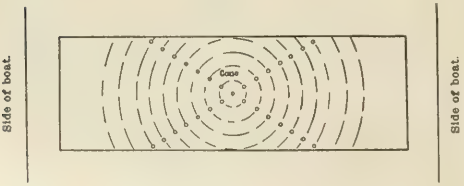
In sampling, a small shovel or garden trowel is used, the total length of which, including the handle, is twelve inches, and it also constitutes a measure. It is the aim to take equal sized samples from each of the points selected. When lump ore or rock is encountered at the point determined by the measure a portion is broken off equal to the amount regularly taken.

In the sampling of the cones, at a point midway between the side and the center of the boat, directly under the edge of the hatch, the first sample is taken and sampling continued one shovel length apart up the surface of the cone, over its apex and down the opposite surface to a corresponding point under the other edge of the hatch. This line is crossed from corresponding opposite points under the hatch as shown in the following sketch. Not more than one-tenth of the total sample is to be taken in the sampling of the cones.

CONE SAMPLING.

Face Sampling.—After a grab has removed from a hatch all the ore within reach and has moved to another hatch, the sampler shall measure two shovel lengths from the side of the boat and start up the exposed face of the ore taking samples one shovel length apart all the way to the top, using a ladder if necessary. The next vertical line is measured four shovel lengths from the first and the samples taken each shovel length apart on this line as before, and so on for each succeeding line across the boat. This is repeated on the opposite ore face, and the entire procedure continued until the ore faces of all the hatches are sampled that the character of the boat and the operation of the grabs will permit. When a bulkhead occurs, only the face opposite to it is to be sampled.

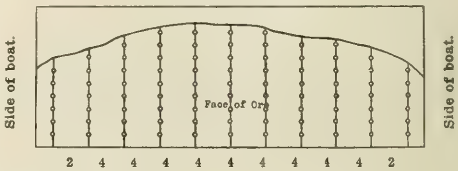
HATCH.



FACE SAMPLING.

Round Sampling.—When the operation of the grabs makes sampling by the face method impracticable, or with boats having twenty-four foot hatch centers, and decks furnishing protection to the samplers, then sampling shall be done while the ore is being removed by the grabs. When five or six feet of the face of the ore have been exposed, the sampler shall enter the hatch and measuring two shovel lengths from the side of the boat or edge of the face, take successive samples up the face one shovel length apart. The next vertical line is measured four shovel lengths from the first, and samples are taken all the way to the top as before, and so on across the entire face of the ore. This procedure is repeated on the opposite face, one-third of the total weight of the sample to be taken in the first round. When all the ore within reach of the grab is removed, the second round is taken, using the measurements as above, and the remaining two-thirds of the sample are secured.

DECK.



Part of the regular sample is to be taken for the moisture sample, and for the fineness sample when such is desired.

CAR SAMPLING AT CONSUMER'S END.

When the ore is received in cars the greatest possible number are represented in the samples, and not less than ten equal sized samples are taken from each car. When cars are loaded with fine ore with the piles in opposite ends, at least five samples are taken from each pile, the first one at the apex of the pile, and the other four at points symmetrically arranged around the sides of the pile, two-thirds of the distance from the apex to the base of the pile or sides of the car. With cars loaded in the center, the system is the same, except that the center of the side of the pile lengthwise of the car, is the first point, the other four being symmetrically arranged around this point.

When the ten points are located in a car, each of them is supposed to represent a definite area, equal to one-tenth of the ore surface of the car. If the car contains all fine ore, then ten equal sized samples are taken, one from each of the points. If the car contains a mixture of fine and lump ore, with varying amounts of each in the areas included in the different divisions, then each area is judged separately and sampled accordingly. The fine and lump ore are taken each in its proper proportion, the former with the trowel, the latter being chipped, or selected small pieces being taken, each about the size of the first joint of the thumb. The combined sample of fine, chipped and selected pieces from

each area, equals the amount taken were it all fine ore. If the contents of the car are all lump ore, the proper sized pieces are chipped from four or five of the lumps in each of the ten areas making forty or fifty pieces from each car, the total amount of chipped pieces from each of the areas equaling the amount that would be taken were it all fine ore. All samples of fine ore are taken from well underneath the surface to obtain the ore in its natural state. A proportionate amount of the main sample is retained in a tightly closed can for the moisture determination.

PREPARATION OF SAMPLES IN GENERAL.

In the preparation of the sample for analysis, the ideal practice is to crush and quarter alternately until the desired quantity with the requisite degree of fineness is attained. A more expeditious and equally efficient method, is to crush the entire sample to the desired degree of comminution, then reduce the quantity by successive quartering as before, until the desired amount remains. It should ever be our purpose to approach as closely as possible to either of these two methods in the preparation of all samples for analysis.

PREPARATION OF SAMPLE AT PRODUCER'S END.

Samples before being quartered are brought into the crusher house where they are dried, if necessary, at 100° C. until the ore can be well mixed. Care must be taken to prevent overheating when other than low pressure steam is used for the purpose, especially with ores containing a large quantity of limonite. When sufficiently dry the larger lumps are crushed, if necessary, so that the entire sample will pass through a half-inch mesh sieve; a finer sieve may be used if desired. The sample is thoroughly mixed on an iron top table, then spread out evenly about three-fourths of an inch in depth and alternately quartered and mixed until one-fourth of the original sample remains. It is now crushed until fine enough to pass a quarter-inch mesh sieve, then mixed and quartered as before until about two pounds remain. It is again crushed until fine enough to pass a twenty mesh sieve, and spread out evenly about three-eighths of an inch in depth. About three ounces of this are taken from all over the pile, with a small spatula, dried in a small pan at 100° C. and crushed on a chrome steel plate, until it will all pass through a hundred mesh sieve. After being thoroughly mixed this is transferred to a bottle, and constitutes the sample for analysis.

The following method for the preparation of the sample is optional. All the ore is passed through a half-inch sieve, thoroughly mixed on a suitable cloth and quartered in the usual way, diagonally opposite portions being rejected until about five pounds remain. The sample is again crushed, if need be, to pass a quarter-inch mesh sieve, and mixed and quartered as before until one and one-half to two pounds remain. After being dried at 100° C. for twenty to thirty minutes, it is crushed to a fineness of twenty mesh, mixed and quartered until about three ounces remain, and the entire sample is crushed on a chrome steel plate and passed through a hundred mesh sieve. This sample is spread out in a shallow pan, dried at 100° C. for thirty minutes, again mixed and transferred to a three-ounce bottle or can for the analysis.

PREPARATION OF SAMPLE AT CONSUMER'S END.

The aggregate sample is dried at 100° C. and crushed before any quartering whatsoever, so that the entire mass will pass through a half-inch mesh sieve. This is reduced by successive quartering and crushing until its weight is from four to eight ounces, and it will then all pass through an eighth-inch-mesh sieve. Or the entire sample is crushed so it will pass through an eighth-inch-mesh sieve, and then quartered as before until from four to eight ounces remain. And this final quantity is then further crushed with a chrome steel bucking board and muller and all passed through a hundred-mesh sieve. A sufficient amount of this powder for all the needs of the analyst is placed in a small air-tight container, dried for one hour at 100° C. and when cool it constitutes the sample for analysis. A separate, larger portion of the same sample is retained for further needs.

IRON.

By the Bichromate or Permanganate Methods.

One or more portions of one-half to one gram of the ore are placed in a beaker, and 5 to 10 cc. of the solution of stannous chloride and 5 to 25 cc. of strong hydrochloric acid are added. This variation in the amount of acid is due, aside from the variations in the weight of sample and the varying solubilities of the ores, to the fact that while in the permanganate method the minimum amount of free acid should be present, with the bichromate method an excess of acid is essential. The beaker is covered with a watch glass and heated gently on the steam bath, or hot plate, until all iron is dissolved, and if the permanganate method is to be used, the volume of the solution is reduced by evaporation so as not to exceed 10 cc. While still hot the stannous chloride solution is added from a burette, drop by drop, until the color due to the ferric chloride just disappears, and then one drop in excess. The solution is diluted to about 350 cc. with cold water, 5 cc. of mercuric chloride solution are added and the solution is thoroughly stirred. From this point the bichromate or permanganate titrations are optional. In the former case, the potassium bichromate solution is added from a burette until a drop of the solution being titrated, added to a drop of the potassium ferricyanide solution on a paraffined plate shows no ferrous iron. In the latter case, 10 cc. of the titrating solution are added for a one-half gram sample, and 20 cc. for one gram. The solution is stirred and titrated with the potassium permanganate. In either case, the number of cc. used multiplied by the respective factor gives the percentage of iron.

If the residue is suspected of containing iron it is filtered off, ignited and fused; the fusion is dissolved in water, acidified with hydrochloric acid, and the solution reduced and titrated as above; or the solution before being acidified is filtered, the ferric oxide on the filter is dissolved in hydrochloric acid and added to the main solution or titrated separately.

SOLUTIONS FOR IRON TITRATIONS.

The stannous chloride solution is made by dissolving 250 grams of the salt in 500 cc. of strong hydrochloric acid, and diluting to 1000 cc.

The mercuric chloride solution is saturated in the cold.

The potassium ferricyanide solution is made fresh each day by dissolving in the proportion of 0.100 gram of the salt in 100 cc. of water.

The potassium bichromate solution is made by dissolving the salt in the proportion of about 8.9 grams to one liter of water, and standardizing with an iron ore, iron wire or

steel, of known iron content. One cc. equals approximately 1 per cent. iron with a one gram sample taken for analysis

The titrating solution is made up in the following proportion to the liter: 90 grams of manganous sulphate are dissolved in 650 cc. of water, 175 cc. of strong sulphuric acid are added, then 175 cc. of phosphoric acid of 1.75 sp. gr., and the solution is filtered if necessary.

The permanganate solution is made by dissolving the salt in the proportion of about 5.7 grams to 1 liter of water and standardizing in the same manner as the bichromate solution. One cc. equals approximately 1 per cent. iron with a one gram sample taken for analysis.

SILICA.

Using One Gram with Hydrofluoric Evaporation.

One gram of the sample is transferred to a porcelain dish, or a beaker, with watch glass cover, and 20 cc. of strong hydrochloric acid are added. A gentle heat is applied until the ore is dissolved and the solution is then evaporated to dryness, unless it has been conclusively shown to be unnecessary.[1] To the residue, which should not be heated above 120° C., 15 cc. of dilute hydrochloric acid (1 part acid to 1 part water) are added, heat is applied until the salts are dissolved and the solution is diluted with hot water. The precipitate is filtered off, washed, ignited at the highest temperature of the blast lamp or muffle furnace for at least five minutes, cooled and weighed. To the residue in the crucible one or two drops of strong sulphuric acid and 5 cc. of hydrofluoric acid are added, and the solution is evaporated to the expulsion of sulphuric acid. The residue is ignited as before and again weighed; the difference between the two weights is silica.

SILICA.

Using One to Five Grams when All or Part of the Filtrate Is Used for the Phosphorus or Other Determinations.

One to five grams of the sample are transferred to a dish (beaker optional) with a watch glass cover, 20 to 50 cc. of strong hydrochloric acid are added, and a gentle heat is applied, without boiling, for about one-half hour. The solution is diluted with an equal volume of water, filtered into another dish of the same size, and the visible iron stain is washed out of the filter paper. This solution containing the bulk of the iron is allowed to go to dryness on the steam bath. The residue is ignited in a platinum crucible, and then fused with about six times its weight of sodium carbonate. The fusion may be leached out of the crucible, but it is found more expeditious to let it cool around the end of a platinum rod, and on again heating the crucible the entire mass adhering to the rod is removed. It is then dissolved in the original filtrate, or placed while still hot in the covered dish, in which the original solution was made and to which about 25 cc. of hot water have previously been added. The small amount remaining in the crucible is dissolved in hot water, and finally in hot dilute hydrochloric acid (1 part acid to 1 part water), and added to the dish containing the fusion, which by this time has been disintegrated by the hot water and acidified with hydrochloric acid; this dish is then placed with the other on the steam bath. When the contents of both dishes are dry, 10 to 15 cc. of strong hydrochloric acid are added to the dish containing the residue of the original filtrate. After heating until the ferric salt is dissolved, the solution is evaporated until the excess of hydrochloric acid is expelled, as is indicated by the first appearance of insoluble ferric chloride on the bottom or sides of the dish. Seven cc. of strong nitric acid are added and heat is applied for about one minute, or until the violent reaction is over. The solution is diluted with cold water and filtered into a suitable flask. This is the procedure if all the filtrate is to be used for the phosphorus determination; but the evaporation of the excess hydrochloric acid and the addition of the nitric acid are dispensed with, if the united filtrates are to be received in a volumetric flask and aliquot portions taken for the other determinations.

[1] This clause is introduced on the insistence of the mine chemists that with certain ores evaporation to dryness is not necessary to obtain all the silica.

To the dish containing the fusion, and which should not be heated above 120° C., just enough dilute hydrochloric acid is added to moisten the residue. Hot water is then added and heat applied until all the salts are dissolved, when the solution is filtered into the same flask with the last filtrate; the combined filtrates should not exceed 150 cc. if the solution is to be used for the phosphorus determination. In this case, the complete washing of the silica is continued in another flask until free from chlorides, and these washings are discarded. The filter and its contents are then ignited and weighed as silica. The filtrate in the flask is reserved for the phosphorus determination, or if in a volumetric flask, for the determinations which follow.

PHOSPHORUS.

By the Fusion Method.

For this determination, five grams of the sample are taken for all ores when the phosphorus content is under 0.100 per cent., two and one-half grams when the phosphorus content is between 0.100 and 0.200 per cent., and one gram when the phosphorus exceeds 0.200 per cent.

An aliquot part of the filtrate, the volume of which should not exceed 150 cc., representing one gram, or two and a half grams of the sample, from the five-gram portion for silica in the volumetric flask, is boiled in a suitable flask for a few minutes with the addition of 10 cc. of strong nitric acid. To this solution, or to the entire filtrate in the flask from the five-gram portion, a slight excess of strong ammonia is added over the amount necessary to precipitate the iron and alumina, and after mixing enough strong nitric acid to dissolve the precipitate with from 5 to 10 cc. in excess.

The solution is heated to a temperature of 80° C., 50 cc. of the solution of ammonia molybdate are added, and the flask is shaken continuously for five minutes. The solution is allowed to stand until the precipitate has subsided. If the yellow precipitate is to be weighed, it is caught on a 9 cm. filter paper that has been dried for at least half an hour at 110° to 120° C. and weighed between watch glasses, washed thoroughly with a 2 per cent. solution of nitric acid, dried for one hour at the above temperature and weighed between glasses; 1.63 per cent of its weight is phosphorus.

If the yellow precipitate is to be titrated by the acid alkali method, the weighing of the filter is dispensed with, the washing with the 2 per cent. nitric acid is continued as before to the complete removal of the iron and molybdenum salts, and then with a 1 per cent. solution of potassium nitrate until free from acid. The filter and its contents

are then transferred to a small flask or beaker and an excess of the standard alkali added. When the precipitate is all dissolved by shaking or stirring, about 150 cc. of water and a couple of drops of a saturated solution of phenolphthalein in alcohol are added, and the solution is back titrated with the standard nitric acid to the disappearance of the color. It is optional to again add the standard alkali, the end point being a faint, permanent, pink color.

The yellow precipitate may also be dissolved in dilute ammonia, and the phosphorus determined by the permanganate titration method as subsequently described. Or it may be dissolved in a hot ammoniacal citrate solution and the phosphorus precipitated as ammonium magnesium phosphate, as hereafter described.

Ammonium Molybdate Solution.—This solution is made in the following proportions: to 225 grams of pure molybdic acid in a suitable flask there is added 500 cc. of water, and then 500 cc. of strong ammonia. When in solution, this is poured into a flask containing 2500 cc. of nitric acid of 1.20 sp. gr., the solution being kept agitated, and three or four drops of ammonium or sodium phosphate solution are added to coagulate the suspended impurities. The solution is kept in a warm place over night or until the supernatant liquid is clear, when it is filtered into a bottle for use.

Stock Solution of Caustic Soda.—145 grams are dissolved in water and the solution is diluted to 2200 cc.; 200 cc. of this solution diluted to 2000 cc. will be of approximate strength.

Nitric Acid.—20 cc. of strong nitric acid are diluted to 2000 cc. These solutions are made exactly agreeing and standardized on steels or ores of known phosphorus content so that each cc. used corresponds to 0.01 per cent. phosphorus, when two grams of the sample are used. This weight has been found the most convenient for steel analysis, and a simple calculation enables it to be used for varying weights of either steel or ore.

PHOSPHORUS

Direct Determination of the Soluble Phosphorus Using the Permanganate or the Acid Alkali Titration.

This method is particularly applicable to ores wherein all or a fairly constant proportion of the phosphorus is soluble in strong acid. The insoluble phosphorus is determined at less frequent intervals, and the amount so obtained added to the soluble gives the total phosphorus.

From one to five grams of the sample, according to the phosphorus content, are placed in a beaker with a watch glass cover, 20 to 50 cc. of strong hydrochloric acid are added and a gentle heat is applied until the ore is dissolved. Two or three drops of nitric acid are added and the solution is boiled a minute or two, and then the excess acid evaporated. The solution is diluted and filtered, the filtrate being received in an 8 to 16 ounce Erlenmeyer flask; the filter and residue are washed with dilute hydrochloric acid (1 part acid to 4 parts water) and water until free from iron discoloration.

Strong ammonia is now added until a slight precipitate persists, or until the iron is completely precipitated, and in either case this is dissolved with strong nitric acid, too great an excess being avoided. The solution is heated to 80° C., 30 to 50 cc. of ammonium molybdate solution are added, the flask is shaken and placed in a warm place to allow the precipitate to subside. The greater part of the supernatant liquid is siphoned off, the remainder being filtered, or the entire solution is filtered. The precipitate is washed with ammonium sulphate solution or a 2 per cent. sulphuric acid solution, until free from iron and molybdenum salts.

The funnel containing the precipitate is transferred to the flask in which the precipitation was made, and the precipitate dissolved in dilute ammonia (1 part ammonia to 3 parts water); the resulting solution should not exceed 25 cc. Eight grams of granulated zinc (20 mesh) are added, then 75 cc. of sulphuric acid (1 part acid to 4 parts water), and the solution is boiled gently until reduction is complete. It is then filtered through glass wool or cotton, the filtrate being received in a beaker, and the flask and filter are washed thoroughly with cold water. The solution is titrated with potassium permanganate until a slight, permanent, pink tint is obtained. From the number of cc. used, the percentage of phosphorus is calculated.

If the acid alkali titration is to be used, the yellow precipitate is washed as before with a 2 per cent. nitric acid solution until free from iron and molybdenum salts, then with a 1 per cent. solution of potassium nitrate until free from acid, and the determination is completed in the regular manner.

SOLUTIONS.

Standard Permanganate.

204.5 grams potassium permanganate,
1 carboy (48 liters) distilled water.

Ammonium Molybdate.

300 grams molybdic acid dissolved in
1200 cc. ammonium hydrate, sp. gr. 0.96, this to be added slowly to
4500 cc. nitric acid, sp. gr. 1.20, keeping the solution agitated.

Ammonium Sulphate.

40000 cc. distilled water,
1100 cc. ammonium hydrate, sp. gr. 0.96,
960 cc. sulphuric acid, sp. gr. 1.84.

Phenolphthalein.

Saturated solution in alcohol.

PHOSPHORUS.

By Ignition of the Insoluble Residue.

One to five grams of the sample in a porcelain dish, with watch glass cover, are digested in a 20 to 50 cc. of strong hydrochloric acid with the aid of a gentle heat. After diluting slightly with cold water, the solution is filtered into another dish of the same size and the precipitate washed free of the visible iron discoloration. The filtrate is rapidly evaporated and while this is in progress, the residue is transferred to a platinum crucible and ignited in a muffle furnace or over a blast lamp. The residue is broken up, reignited for a few minutes, then transferred into the original filtrate and the solution is evaporated to dryness.

Fifteen cc. of strong hydrochloric acid are now added and the solution is evaporated until ferric chloride begins to separate in the solid state. To the covered dish, 7 cc. of strong nitric acid are added and heating is continued for about one minute. The solution is diluted with cold water and filtered into a suitable flask. The filter and precipitate are washed with a 2 per cent. nitric acid solution until the iron discoloration is removed.

With unknown ores, and at regular intervals with

all ores, as a check, the insoluble residue is fused with sodium carbonate. The fusion is dissolved in dilute hydrochloric acid (1 part acid to 1 part water), and the solution is evaporated to dryness. The residue is redissolved in dilute hydrochloric acid and the solution is filtered into the main filtrate, which has also been evaporated to dryness, and the residue treated as described in the previous paragraph after the evaporation to dryness. The filtrate, or the combined filtrates in the flask are made ammoniacal, and the precipitate is dissolved in strong nitric acid with 5 to 10 cc. in excess. The solution is brought to a temperature of 80° C., 50 cc. of ammonium molybdate solution are added and the flask is shaken for five minutes.

When the precipitate has subsided, it is filtered off and washed with a 2 per cent. solution of nitric acid. From this point the yellow precipitate may be weighed, or titrated by the acid alkali or permanganate methods as previously described, or dissolved, reprecipitated, and weighed as magnesium pyrophosphate in the following manner.

The yellow precipitate is dissolved on the filter with hot ammonium citrate solution (175 cc. strong ammonia to 325 cc. water containing 25 grams citric acid), the filtrate being received in a No. 0 beaker. The filter is washed several times with hot water, then 5 to 10 cc. of magnesia mixture (100 grams magnesium sulphate plus 300 grams ammonium chloride in 800 cc. hot water plus 400 cc. strong ammonia) are poured through the filter. The filtrate in the small beaker is thoroughly mixed and allowed to stand for at least three hours, and if possible over night. The precipitate is filtered off, washed with dilute ammonia (1 part ammonia to 4 parts water), ignited at a low temperature until the carbon of the filter is destroyed, then at the highest temperature of the muffle furnace or burner, cooled and weighed as magnesium pyrophosphate containing 27.84 per cent. phosphorus.

PHOSPHORUS.

When Titanium is Present.

Two grams of the sample are intimately mixed with eight to ten times its weight of sodium carbonate in a large platinum crucible and fused over a blast lamp, the fusion being maintained at the highest temperature for fifteen to twenty minutes. The fusion is then transferred to a beaker containing hot water and thoroughly disintegrated; the solution is then filtered and the residue washed with hot water, or preferably with a 1 per cent. solution of sodium carbonate. As an extra precaution, not deemed necessary in every-day work, the residue may be ignited until the filter is destroyed, crushed in the crucible, fused, disintegrated and filtered off as before, the filtrates being combined. The filtrate, or the combined filtrates are acidified with hydrochloric acid and evaporated to dryness. The residue is moistened with dilute hydrochloric acid, dissolved in hot water and the solution filtered into a suitable flask.

The filtrate is made ammoniacal, then strong nitric acid is added with from 5 to 10 cc. in excess. The solution is brought to a temperature of 80° C., 50 cc. of ammonium molybdate solution are added, the flask is shaken for five minutes, and the phosphorus determined by any of the methods previously described.

When it is desired to separate the phosphorus from the large amount of sodium salts in the filtrate after the evaporation to dryness, a weighed amount of iron, about 0.05 gram, of known phosphorus content, and in the ferric condition, is added and precipitated in the hot solution with ammonia. The precipitate is filtered off, dissolved in warm, dilute nitric acid, and if the resulting filtrate is somewhat cloudy from particles of filter paper in suspension, and it is desired to remove them, it is refiltered after the addition of a little paper pulp. This filtrate is now made ammoniacal, 5 to 10 cc. excess nitric acid are added, and the determination is completed as above described.

ALUMINA.

Phosphate Method.

For this determination the hydrochloric acid filtrate from the silica of one gram of the sample, or the hydrochloric acid solution of the precipitated iron and alumina from the gravimetric determination of manganese is used. To the cool solution diluted to about 400 cc. in a No. 5 beaker, 30 cc. of a 10 per cent. solution of ammonium phosphate are added, and then ammonia until a faint, permanent precipitate is formed. One and one-half cc. of strong hydrochloric acid are now added, the solution is stirred until the precipitate is dissolved, and 50 cc. of a 20 per cent. solution of sodium hyposulphite are added. The solution is heated just to the boiling point, at which 8 cc. of strong acetic acid and 15 cc. of a 20 per cent. solution of ammonium acetate in the same measure are added, and the boiling is continued ten minutes. The precipitate is allowed a few minutes to subside, is filtered off as quickly as possible and washed ten times with hot water. The filter and its contents are ignited at a low temperature until the carbon is destroyed, then at the highest temperature of the muffle furnace, cooled and weighed as aluminum phosphate, 41.85 per cent. of which is alumina.

ALUMINA.

Ether Method.

One to five grams of the sample are placed in an 8 ounce beaker and dissolved in 20 to 50 cc. of strong hydrochloric acid with the aid of a gentle heat. The solution is diluted and filtered, the residue washed, and the filtrate evaporated to dryness. The residue on the filter is ignited in a platinum crucible, 2 to 6 drops of sulphuric acid (1 part acid to 1 part water) and 5 to 10 cc. of hydrofluoric acid are added and the solution is evaporated to dryness. The residue in the crucible is fused with one-half gram of potassium or sodium bisulphate and dissolved in 10 cc. of dilute hydrochloric acid (1 part acid to 1 part water). The residue from the original filtrate, after its evaporation to dryness, is dissolved in 20 to 30 cc. of hydrochloric acid, 1.13 sp. gr., cooled and transferred to a separatory funnel, 40 to 100 cc. of ether are added and the funnel is shaken for one minute, the solution being kept cool. The acid layer is drawn off into an 8 ounce beaker, and to this is added the solution obtained from the treatment of the insoluble residue. The combined solutions are heated until the ether is driven off, a few crystals of sodium or potassium chlorate are added, and the heating is continued until free chlorine is expelled. The solution is diluted to about 75 cc., ammonia is added until a slight precipitate persists, then 10 cc. of a 20 per cent. solution of ammonium acetate. The solution is boiled about one minute and filtered; the precipitate is washed

with hot water, then dissolved in warm dilute hydrochloric acid. After being diluted to about 75 cc. and a slight excess of ammonia added, the solution is boiled, filtered and the precipitate washed as before. The combined filtrates are reserved for the determination of manganese, lime and magnesia. From this point, the alumina may be determined by either of the following methods:

The precipitate is ignited, and weighed as oxides of iron, alumina and phosphorus. The ignited oxides are dissolved in 3 cc. of stannous chloride and 10 cc. of strong hydrochloric acid, and the iron is titrated with a weak bichromate solution, 1 cc. of which is equal to 0.2 per cent. iron. Or the precipitate is fused with sodium carbonate, the fusion is dissolved in hydrochloric acid and the iron titrated as above. The iron calculated as the sesquioxide, plus the phosphorus as pentoxide is deducted from the total weight of the precipitate, leaving the alumina.

Or the filter and precipitate are ignited at a low temperature until the carbon is destroyed. The precipitate is crushed in the crucible and thoroughly fused with about 5 grams of sodium carbonate. The fusion is dissolved in hot water, a little paper pulp is added to reduce any manganese that may be present, the residue is filtered off and washed. The filtrate received in a small beaker is acidified with hydrochloric acid, heated to boiling, and ammonia is added in slight excess. After boiling for a minute or two, the precipitate is filtered off, washed with hot water, ignited and weighed. This weight minus the weight of the phosphorus as pentoxide is alumina.

MANGANESE.

Gravimetric Method.

The filtrate from the one-gram portion for silica, or an aliquot part of the filtrate, equal to one gram of the ore, from the five-gram portion for silica in the volumetric flask, is boiled for a few minutes in a No. 5 beaker with the addition of 10 cc. of strong nitric acid. A basic acetate separation is then made as follows. The solution is diluted with cold water to about 150 cc. and the greater part of the free acid is neutralized with strong ammonia, then cautiously with dilute ammonia (1 part ammonia to 4 parts water) with vigorous stirring until a faint precipitate persists. The solution is then diluted with hot water to about 400 cc. 25 cc. of a 20 per cent. solution of ammonium acetate are added, the solution is heated to boiling and boiled about one minute. After the precipitate has subsided, the solution is filtered through a 185 mm. filter on a 4-inch ribbed funnel into a No. 6 beaker.

When the manganese is under one per cent., only one basic acetate separation is made and the precipitate is washed several times with hot water. If over one per cent., the precipitate is washed but once, then dissolved on the filter in hot, dilute hydrochloric acid and the basic acetate separation made as before, except that the dilution before precipitating need not be so great. The filtrate and washings, or the combined filtrates in this determination, or from the iron and alumina in the ether alumina method are heated to boiling and 25 cc. of strong ammonia added, and then cautiously about 1 gram of ammonium persulphate. One gram is sufficient to precipitate the manganese in any iron ore. The solution is boiled about ten minutes and the precipitate filtered off, washed with hot water, ignited at a gentle heat and then at the highest temperature of the muffle furnace or blast lamp, and weighed as mangano-manganic oxide, containing 72.05 per cent. manganese. This precipitate may be dissolved before or after ignition, reprecipitated, and weighed as manganese pyrophosphate.

The ignited precipitate of mangano-manganic oxide is usually contaminated with a small amount of silica sufficient to cause an appreciable error in a small percentage of manganese. In this case it is dissolved in the crucible in warm, dilute hydrochloric acid; the residue, if any, is filtered off, washed, burned and the weight obtained is deducted from the previous weight.

The precipitate of iron and alumina on the filter obtained in this determination is to be retained for the determination of alumina by the phosphate method.

MANGANESE.

Volhard's Method.

One to two grams of the sample are placed in a No. 2 beaker with cover, 15 to 25 cc. of strong hydrochloric acid are added, and heat is applied until the ore is dissolved. Five cc. of nitric acid or a few crystals of potassium chlorate are now added, and the solution is boiled until nitrous fumes or free chlorine are expelled. Evaporation is continued to the expulsion of free acid, the solution is diluted to about 100 cc. and washed into a volumetric flask. Zinc oxide emulsion is added in excess, the solution is diluted to the mark and mixed thoroughly; the precipitate is allowed to subside and an aliquot portion is decanted off, equal to one-half or one gram of the ore. For ores low in manganese, the solution is made slightly turbid with zinc oxide emulsion to coagulate the manganese dioxide set free in the titration. The solution is heated to boiling and titrated with permanganate until a faint, pink color persists. Or, after the dilution to about 100 cc., the solution is washed into a half liter flask, an excess of zinc oxide emulsion is added as before, the solution is heated to boiling and titrated directly in the presence of the iron precipitate.

Strength of permanganate solution for iron ores: 1 cc. equals 0.1 per cent. manganese, standardized on iron ore of about one-half per cent. manganese content.

For manganese ores, the procedure is the same up to the removal of the free acid and the addition of zinc oxide emulsion, when the solution is diluted to the mark in a 500 cc. volumetric flask and mixed. Then 50 cc. are transferred to a flask, diluted to about 250 cc., heated to boiling, and titrated as before. No zinc oxide emulsion need be added here, the voluminous precipitate of manganese dioxide acting as coagulant.

Strength of permanganate solution for manganese ores: 1 cc. equals 0.3 per cent. manganese, standardized on manganese ore of known manganese content.

MANGANESE.

Color Comparison or Titration Method.

One gram of the sample in a porcelain dish, or beaker, is warmed after the addition of 25 cc. of strong hydrochloric acid and 5 cc. of strong sulphuric acid, and when in solution, the heating is continued until fumes of sulphuric acid appear. The solution is allowed to cool, 25 cc. of water are added, heat is applied until the salts are dissolved and the solution is transferred to a 50 cc. volumetric flask, diluted to the mark

and mixed. If the color comparison method is to be used, the solution should be poured through a dry filter after mixing; if the titration method is to be used, the filtration may be omitted. With a pipette 10 cc., equal to 0.2 gram of the ore, are transferred into a 1-in. by 8-in. test tube, if for comparison, or into a 150 cc. Erlenmeyer flask, if to be titrated Fifteen cc. of the nitrate of silver solution are added, the solution is heated over a flame or in a water bath, and about one gram of ammonium persulphate is added. The reaction takes place equally well in a nitric or sulphuric acid solution or a mixture of the two. The essential point is the presence of a sufficient amount of silver nitrate. As soon as the formation of the permanganic acid is well under way, the test tube or flask is removed from the source of heat and placed in a cold water bath. This solution may be compared against the color obtained from an ore or a steel of known manganese content, in the latter case by dissolving 0.2 gram of the steel in 10 cc. of nitric acid of 1.20 sp. gr., adding 15 cc. of the silver nitrate solution and the persulphate as above.

If the solution in the 150 cc. Erlenmeyer flask is to be titrated, it is diluted to about 100 cc., 7 cc. of a 0.2 per cent. solution of C. P. sodium chloride are added and the sodium arsenite solution is run in until the color is just discharged.

If the insoluble residue is suspected of containing manganese, it is filtered off, burned, 2 or 3 drops of sulphuric acid (1 part acid to 1 part water) and about 5 cc. of hydrofluoric acid are added and the solution is evaporated until sulphuric acid fumes appear; 5 cc. of the same dilute sulphuric acid are added, and the crucible is warmed till the residue is in solution, when it is added to the main solution.

The stock solution of silver nitrate is made in the proportion of 66.66 grams of the salt to the liter. Twenty cc. of this solution are diluted to one liter for use; each 15 cc. contains 0.02 gram of silver nitrate.

The sodium arsenite solution is made by boiling 10 grams of arsenious acid until dissolved in an aqueous solution of 30 grams of sodium carbonate and diluting to 1 liter. About 125 cc. of the stock solution are diluted to 2000 cc., and this solution is standardized on steels or ores of known manganese content so that 1 cc. equals 0.1 per cent. manganese on a 0.2-gram sample.

MANGANESE.

Peroxide Reduction Method.

One-half to three grams of the sample in a beaker are digested in 20 to 50 cc. of strong hydrochloric acid. If the insoluble residue is suspected of containing manganese, a few drops of hydrofluoric acid are added, and the solution is evaporated almost to dryness. Manganese-free glass must be used if hydrofluoric acid is employed. Seventy-five cc. of strong nitric acid are added, the solution is boiled until clear, the manganese is precipitated as dioxide by the addition of a slight excess of potassium chlorate, and the boiling is continued for about five minutes. The solution is cooled, diluted to about 300 cc. with cold water, and a definite amount of hydrogen peroxide solution is added from a pipette. After the reduction of the dioxide, the excess of hydrogen peroxide is determined by titration with standard potassium permanganate solution. The value of the peroxide solution in terms of permanganate is determined, and from the total volume of peroxide used, less the excess determined by the permanganate titration, the percentage of manganese is calculated.

The relative value of these two solutions is determined as follows: About 60 cc. of strong nitric acid are boiled for about five minutes in a beaker, then cooled and diluted to about 300 cc. To the cold solution, a definite amount of the peroxide solution is added and titrated with the standard permanganate.

The hydrogen peroxide solution is made by diluting one pound of hydrogen peroxide to 9000 cc., containing 200 cc. of strong sulphuric acid.

The permanganate solution contains 1.7375 grams per liter and is standardized against an ore of known manganese content.

LIME.

The filtrate from the persulphate or bromine precipitation of the manganese, after the basic acetate or ammonia separation of the iron and alumina, is heated to boiling in a No. 6 beaker, 10 cc. of strong ammonia and 5 cc. of a saturated solution of ammonium oxalate are added, and the heating is continued until the volume of the solution is reduced to about 150 cc. When the lime is low it is essential that the evaporation be continued to this point to insure complete precipitation. Five cc. of strong ammonia are now added and the solution is boiled for about ten minutes. The precipitate is then filtered off, washed with hot water, burned and weighed as calcium oxide. In normal ores when the lime and magnesia are low, only the first few washings are allowed to flow into the filtrate, the object being to keep the filtrate as concentrated as possible for the magnesia determination which follows. The calcium oxide is also liable to be contaminated with a small amount of silica and when extreme accuracy is desired, the ignited and weighed precipitate is dissolved in warm, dilute hydrochloric acid and the solution is evaporated to dryness. The residue is dissolved in dilute hydrochloric acid, the silica is determined and deducted from the previous weight.

If the lime is to be titrated, it is dissolved on the filter in 25 cc. of hot, dilute sulphuric acid (1 part acid to 4 parts water), the solution is diluted with 150 cc. of hot water and titrated with permanganate of such strength that 1 cc. equals about 0.100 per cent. lime.

MAGNESIA.

The filtrate from the calcium oxalate, which should not exceed 200 cc. in volume, is made slightly acid with strong hydrochloric acid, and 5 cc. of a 10 per cent. solution of ammonium phosphate are added, then to the cool solution, 25 cc. of strong ammonia, drop by drop, with continuous stirring during the addition. The solution is stirred at intervals for two or three hours, or continuously on a machine for one hour, and if permissible it is allowed to stand in a cool place over night. The precipitate is filtered off, washed thoroughly with dilute ammonia (1 part ammonia to 4 parts water), ignited at a low temperature until the filter is destroyed, and finally at the highest temperature of the muffle furnace or blast lamp, and weighed as magnesium pyrophosphate containing 36.24 per cent. magnesia.

SULPHUR.

Fusion Method.

One gram of the sample is intimately mixed in a capacious platinum crucible with about ten grams of sulphur-free

sodium carbonate, and not more than a half gram of potassium nitrate. The crucible is heated cautiously over a blast lamp until the fusion is quiet, the last few minutes of the fusion being at the highest temperature of the blast. If sulphur bearing gas is used, the contents of the crucible must be protected from the flame gases with a suitable shield. The fusion is completely disintegrated in hot water, to which a few drops of alcohol may be added to reduce and precipitate any manganese present. The solution is filtered and the residue washed with hot water, or preferably with a 1 per cent. solution of sodium carbonate.

To the filtrate, the volume of which is about 150 cc., there is cautiously added a slight excess of hydrochloric acid. The solution is heated to the boiling point, 5 cc. of a 10 per cent. solution of barium chloride are added, and the beaker is placed on the steam bath or hot plate until the precipitate has subsided. The precipitate is then filtered off, washed with hot water till free from chlorides, burned in an open crucible and weighed; 13.73 per cent. of the weight is sulphur.

If the precipitate is suspected of containing silica, which is rarely the case, it can be purified after ignition by adding a drop of sulphuric acid and 2 or 3 cc. of hydrofluoric acid, evaporating and igniting as usual.

If sulphur-free sodium peroxide is used for the decomposition of the ore in place of the sodium carbonate and niter, the fusion is made in a nickel crucible with about 5 grams of the peroxide; the remainder of the treatment is the same.

SULPHUR.

Wet Method.

Five to ten grams of the sample in a porcelain dish or beaker, with a watch glass cover, are dissolved in 50 to 100 cc. of aqua regia (1 part nitric acid to 9 parts hydrochloric acid) and the solution is evaporated to dryness. The residue is dissolved in 20 to 40 cc. of strong hydrochloric acid and the solution evaporated until the first appearance of insoluble ferric chloride. This is dissolved by the addition of a slight excess of strong hydrochloric acid, the solution is diluted to about 75 cc., and filtered into a suitable beaker, the residue being washed with hot water and the least possible amount of dilute hydrochloric acid.

If the insoluble residue is suspected of containing sulphur compounds insoluble in aqua regia, it is fused with the least possible amount of sodium carbonate and niter, as previously described in the Fusion Method for Sulphur. The fusion is disintegrated in hot water, the solution is filtered, acidified with hydrochloric acid and added to the main filtrate, or the sulphur may be estimated separately.

The filtrate is heated nearly to boiling, and after the addition of 5 cc. of a 10 per cent. solution of barium chloride it is again evaporated until a film of ferric chloride appears. This is dissolved by the addition of a few drops of strong hydrochloric acid and, with a wash bottle, a stream of cold water is forced into the solution until its volume is from 175 to 250 cc. It is then set aside in a cool place over night. The precipitate is filtered off, washed with hot water and dilute hydrochloric acid until free from iron, burned and weighed as usual.

IGNITION LOSS.

One gram of the sample is placed in a platinum crucible with a tightly fitting cover and ignited at a bright red heat for fifteen minutes. It is then allowed to cool in a desiccator and weighed. This is repeated with five minutes' ignition until constant weight is obtained.

MOISTURE.

A portion of the entire sample reserved for the moisture determination, in either case not less than two kilograms, is transferred to a suitable pan and weighed, dried at 100° C. until constant weight is obtained and the percentage of moisture calculated.

REPORT OF THE COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY APPOINTED TO CO-OPERATE WITH THE NATIONAL CONSERVATION COMMISSION.

In May, 1908, a meeting of the governors of the different states was held at the White House in Washington to consider the conservation of our rapidly wasting natural resources. Following this meeting, a commission was appointed by the President of the United States to investigate the subject, and the principal scientific societies of the United States were invited to coöperate with it. The committee of the American Chemical Society, appointed in response to this invitation, now has the honor to submit the following preliminary report.

On December 8, 9, and 10 the National Conservation Commission met in Washington in joint conference with the delegates of other organizations and the governors of more than twenty states. The commission, in its elaborate investigations, had, so to speak, taken stock of our natural resources, and its report, therefore, was essentially statistical in character. It had estimated the magnitude of each particular resource, and had studied the rate of consumption of such substances as lumber, coal, iron, etc. It discussed the wastage of the land by preventable erosion, and its effects not only upon agriculture but also in reducing the navigability of streams. Questions like these were treated at considerable length, and their general character is all that need be mentioned just here. The data of the commission were mainly classified under four headings, namely, minerals, forests, lands, and waters, and under each one the evils to be remedied were pointed out with all the emphasis and clearness which the statistical method of investigation made possible. The commission cleared the ground for study into the prevention or limitation of future waste; and the problem of conservation can now be taken up in a more intelligent manner than has been possible hitherto. We now know better than ever before what the evils and dangers really are; the next step is to discover remedies, and then, finally, to apply them. The public attention has been aroused; the people of the country are awakening to the necessity of greater prudence and economy in the use of our resources, and definite lines of action can now be laid down with a reasonable probability that they will be followed. Fortunately, the reports of the commission are neither sensational nor unduly pessimistic; the results of their conferences are presented seriously, and in such a manner as to compel consideration; they are therefore all the more likely to produce permanent effects of great benefit to the American people. The utterances of the mere alarmists rarely carry conviction, but disclosures like these made by the Conservation Commission can not be disregarded.

Up to the present moment chemistry has had little to do with the investigations of the commission. Henceforward the chemist must be called upon in many ways, for the waste of resources is often preventable by chemical agencies. Chemistry has already done enough to prove its potency, and its influence is felt in every branch of industry. Adopting the classification of the commission, we shall find the chemist active under every heading. Under minerals, we must note that metallurgy is essentially a group of chemical processes by which the metals are separated from the ores, a separation which may be either wasteful or economical. Within recent years, within the memory of members of this society, the available wealth of the world in metals has been enormously increased. By the cyanide process for extracting gold, ores are now profitably worked which were formerly worthless, and at the same time the demand for mercury has been decreased. The Bessemer process for steel-making, now also modified for use in copper smelting, is purely chemical, and its later modification, the Gilchrist-Thomas process, applies similar principles to phosphatic ores, which were previously of little value. Furthermore, in the last-named process, phosphatic slag is produced, which is useful as a fertilizer and helps to relieve the drain upon our rapidly wasting supplies of phosphate rock. Chemists are now studying, with much success, the problem of preventing corrosion in iron, a research which will prolong the life of iron structures and thereby reduce the waste of ore. The use of coal slack by briquetting methods is largely based upon chemical investigations; the salvage of by-products from coke ovens, such as tar and ammonia, is wholly due to chemical research; coal is further economized by the study of boiler waters and the consequent prevention of boiler scale. Even inferior coals, lignites, are now converted into what is known as producer gas, and so are transformed into the best kind of fuel. Petroleum is refined by chemical means, and every fraction of it is saved, either as illuminating oil, as gasoline, as a lubricant, as vaseline, or as paraffin. These are all notable achievements, but greater are yet to come. Enormous quantities of valuable substances are thrown into the atmosphere in fumes from smelters, which should, and probably can be, partly saved. Electrochemistry is rapidly developing a large group of new industries, making such metals as aluminum, magnesium, and calcium available for use, and it is reaching out into other fields of electrometallurgy in which electric heat, generated by water power, will be used for smelting other metals, thereby reducing the consumption of coal.

In forestry also, the influence of the chemist is distinctly felt. The sprays, used for destroying noxious insects, are chemical preparations. The manufacture of wood alcohol is a chemical process, which may be either wasteful or economical. Turpentine is now produced wastefully, but the waste can be diminished by careful refining, and furthermore, the chemist can aid in discovering substitutes for it. Substitutes for tan bark are also to be sought for by means of chemical investigations. Another distinctively chemical operation is the preparation of wood pulp for paper-making, a process which is now wasteful in the highest degree. It is estimated that for every ton of pulp now made by the sulphite process, more than a ton of waste material is allowed to drain away into our streams. How to make this material useful is a chemical problem, and so also, in great part, is the investigation of other, now useless fibers, which may replace the more valuable wood. The preservation of wood from decay is still another art in which chemistry is predominant.

In preserving the fertility of our land, chemistry has an important part to play. Our knowledge of fertilizers, of the food on which crops can thrive, is entirely chemical so far as accuracy is concerned, and must be applied in accordance with chemical principles. A fertilizer which is useless, and therefore wasted on one soil, may be needed on another. Certain fertilizers, like the Stassfurt salts, Peruvian guano, the Chilean nitrates, and phosphate rock are limited in quantity, and their future exhaustion must be considered now. What shall replace them in the future? Already processes have been devised for fixing the nitrogen of the atmosphere and rendering it available for plant food. Saltpetre and other nitrates can be and long have been made from waste materials such as old mortar and animal refuse. The phosphatic slags have been mentioned in connection with metallurgical processes. These sources of fertility are important, but greater still is the source found in our municipal sewage. The problem of its salvage has been worked out in some localities, but in the United States the people are only beginning to be aroused to its importance. Enormous masses of material, easily available for fertilizing purposes, now drain into our rivers or directly into the sea. Another question, now under investigation, is the possibility of using our common feldspathic rocks in fine powder, to replace the potassium withdrawn by plants from the soil.

The relations between the chemical composition of water and the conservation of natural resources are of intimate and fundamental importance and some of them have been mentioned under other headings. The rate at which the land surface of the United States is being transported to tide water has recently been estimated by means of chemical analyses of river water coupled with determinations of stream flow, and the results of the computations will doubtless assist considerably in studying soil erosion and the impoverishment of agricultural lands. In steam making the chemical quality of the water supply is an appreciable factor in fuel consumption, a subject to which reference has already been made. The scale that forms on the boiler shell and tubes, when water containing incrustants is used, is a poor conductor of heat and, consequently, causes increased expense for fuel. By detailed study of the chemical composition of available boiler waters, it is possible to select a supply having a minimum amount of incrusting, corrosive, and foaming constituents, thereby effecting appreciable economy in fuel. Chemical investigation of methods for purifying water supplies, not only for boilers but for paper manufacture, soap-making, and other great water-consuming industries, will enable manufacturers to make new and greater saving in many raw materials other than fuel.

Stream pollution by industrial refuse and by sewage is a source of enormous waste in our natural resources. The subject has been for many years a field of research for industrial, sanitary, and biological chemists in the United States, and their investigations have resulted in the improvement of manufacturing processes, the utilization of wastes, the purification of sewage, and the protection of domestic water supplies. When the presence of deleterious

substances in our river and lake waters has caused loss of fish life and the destruction of oyster beds, the chemist and the biologist have detected the harmful ingredients and have suggested methods for their removal. River silt, an important source of detriment to navigation, is also estimated by the chemist. It has been fully demonstrated that the prevention of stream pollution lies not alone through injunctions and other legal prescriptions but also in using waste materials or, when that is not possible, in rendering them harmless. The chemist has much to do in protecting and preserving the quality of our water supply. Upon that, in very great measure, depends the preservation of our highest resource, human life. Polluted waters distribute typhoid fever and other dangerous diseases, and so cause losses which should be, and really are, preventable.

The foregoing illustrations are enough to show, for present purposes, the intimate connection between chemistry and the study of conservation. They also bring out the fact that the classification adopted by the National Commission, although admirable for statistical research, is not final, and that it needs to be supplemented by a different subdivision of the data. The facts to be investigated often fall under more than one heading of the classification, and actually interlock in every conceivable manner. To operate a placer mine, for example, abundant water is needed, while a deep mine requires timber for its shafts and levels. In building and occupying a house one covers land, uses lumber, brick, stone, and iron, introduces water supply, and burns fuel. In short, every phase of the conservation question affects the interests of everybody. If the investigation of our natural resources is to be made effective, it must be applied to individual industries, and in order to do that another scheme of classification would seem to be necessary. Such a scheme we venture to outline, but very briefly.

At the outset the problem can be divided into two parts, one relating to sources of energy, the other to material substances. The two are not really separable, but may advantageously be considered separately.

In the first place, the energy available for industrial uses may be classified under three heads, as follows: First, inexhaustible energy, such as solar radiation, wind power, tidal power, and, with certain limitations, the power furnished by flowing streams. Second, reproducible or renewable energy, like the power supplied by horses and other domestic animals. Wood, regarded as fuel, also falls under this heading, for forests can be artificially grown. Third, the exhaustible energy represented by mineral fuel, like natural gas, petroleum, and coal, which, once used, is gone forever. Under this classification the practical problems are, to economize the exhaustible energy, to encourage the development of renewable energy, and to discover new methods of using the inexhaustible energy.

Exactly the same classification applies to material substances. Some, like sea salt, limestone, and clay are, humanly speaking, inexhaustible. Agricultural and forest products are reproducible, some of them year by year. The metallic ores and such useful minerals as phosphate rock are, however, exhaustible, and need to be conserved.

With the aid of this very simple classification it becomes possible to analyze a specific industrial problem in such a manner as to make evident its factors of waste or economy. For example, sea salt is inexhaustible, and may be extracted by solar evaporation, which is a use of inexhaustible energy. Agricultural products are renewable, and their production chiefly requires the renewal energy of men and animals. But the smelting of metallic ores, as now conducted, involves the use of exhaustible material both as ore and as fuel.

In most industries, however, the two sets of considerations are combined. Portland cement, for example, is made from inexhaustible substances, but is burned with exhaustible fuel. The latter factor in the industry, therefore, is the one to be carefully considered, while the first factor is negligible. Taking industry by industry we shall find that this condition of affairs is general, and that each one must be studied by itself with reference to its inexhaustible, reproducible, and exhaustible elements. In doing this a clear notion can be obtained as to the real needs of a given industry, and our attention can then be concentrated upon those features of it which particularly demand economy. We shall be able to locate evils with greater accuracy; to diagnose the industrial diseases, so to speak, and then to look intelligently for remedies. Many of the remedies must be sought for along chemical lines of research, which will develop economical processes of manufacture, utilize materials that are now wasted, or substitute cheap for costly substances. Cheap and costly, however, are words which need qualification. A substance or a process which is cheap to-day may be in reality wasteful with a temporary reduction in price at the cost of some permanent economy. For our purposes the two words imply a deeper discrimination than is carried by their ordinary use. Temporary efficiency and cheapness are to be discountenanced, while permanent economy for the benefit, not only of the nation but of the whole human race, is to be encouraged. This principle is sound, but its practical applications will involve many difficulties, and develop many conflicts with special interests. Like all ideals it can not be realized absolutely, but it represents a standard of action towards which we must move, even though the ultimate goal of perfection may never be attained. Evils can be mitigated, although they may not be entirely removed.

The American Chemical Society now numbers more than four thousand members, scattered through all the states and territories of the union and represented in every one of our great productive industries. These chemists are at the same time progressive and conservative in their work, for they are both discovering new utilities and protecting old ones from loss. We believe that every member of the organization is necessarily in sympathy with the great forward movement for economy, and that in our society the National Conservation Commission will find a most powerful and willing ally.

Signed, F. W. Clarke,
H. W. Wiley,
C. H. Hertz,
S. W. Parr,
R. B. Dole.

LIGHT NAPHTHA AS A TURPENTINE ADULTERANT.

Mr. A. E. Paul states in his very interesting article on "Turpentine and its Adulterants," in the January number

of this Journal, that very light naphtha is never employed for purposes of adulteration.

I would say that I have come across several samples of so-called turpentine—sold as "pure"—which contained a high percentage of light naphtha, otherwise "gasoline."

R. H. Acott.

A PECULIAR CHLORATE EXPLOSION.[1]

A short time ago Dr. McKenna read a paper before this section on the hazard of explosives in which he gave account of several explosions caused by chlorate of potash. Since then several unusual cases of this kind have come to my notice. The facts as reported to me are as follows: A company in this city, makers of small castings, has been purchasing kegs from a second-hand dealer. These were used for packing castings for shipment.

In the first case some of these kegs containing ingots of aluminum and zinc were being unloaded on a wharf when a keg took fire. The laborers supposed the kegs contained grains of powder and wanted to throw the entire lot into the river. The owners of the foundry could not account for the fire but thought some mysterious property of the zinc and aluminum might have caused it. No further investigation was made in this case.

A few weeks ago a shipment of small iron castings was made to a neighboring city. When unloading one of the kegs from a truck, a slight explosion occurred; two men were slightly burned while the keg burned rapidly enough to heat the castings quite hot. On investigation it was discovered that this keg had been obtained from a dye works and had contained chlorate of potash. The second-hand dealer claimed this lot of kegs had been thoroughly cleaned before delivery to the iron works but however that may have been either some chlorate had lodged in the crevices and escaped detection or else the wood had become saturated with it from standing in a damp place. The jolting of the castings struck a spark which fired the mixture of chlorate and wood.

Chlorate of potash is used by dyers and in this vicinity; where there are many dye houses, there must be a large number of these kegs to be disposed of in some manner.

Fortunately all the fires of this kind of which I am aware occurred in the open air and did no damage. They might just as easily have occurred in a warehouse or on shipboard. In fact the foundry using these kegs, ships castings abroad and it might be a very serious matter to have a fire of this sort in the hold of a ship.

Evidently purchasers of second-hand kegs have another danger to be guarded against, and we have another possible cause for fires of mysterious origin. George C. Davis.

A NEW COMBUSTION PIPETTE.

My experience of several years in gas analysis has led me to construct a new form of combustion pipette that I have found superior to any other form I have yet used My duties as Gas Analyst of Sioux City have afforded me ample opportunity to test this apparatus, and it is with assurance that this form will be of interest to those engaged in gas analysis and of decided practical value that I bring the pipette to public notice.

[1] Read before the Philadelphia Section, American Chemical Society.

The combustion tube—see figure— resembles the familiar Hempel burette with the exception that the cylinder is open to the full diameter of the tube at the base. This opening is closed by means of a stopper through which

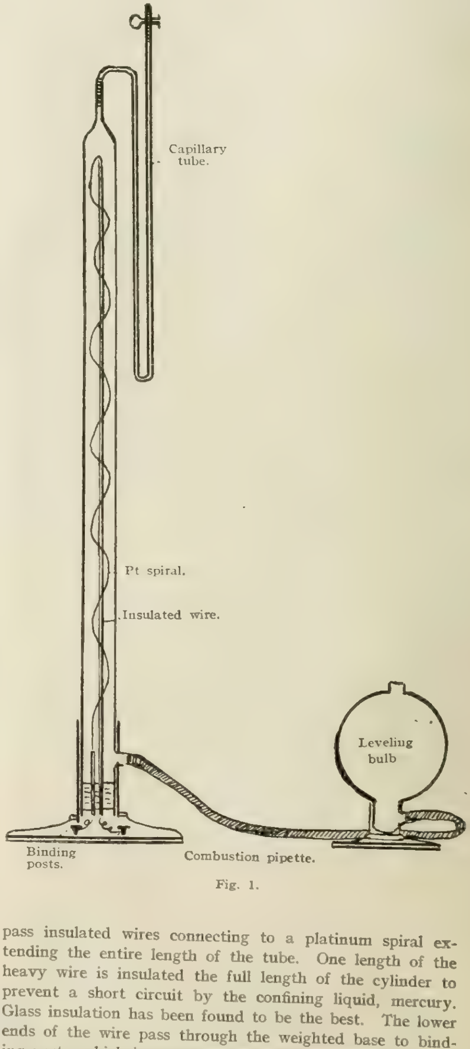


Fig. 1.

pass insulated wires connecting to a platinum spiral extending the entire length of the tube. One length of the heavy wire is insulated the full length of the cylinder to prevent a short circuit by the confining liquid, mercury. Glass insulation has been found to be the best. The lower ends of the wire pass through the weighted base to binding posts, which in turn may be easily connected to a battery. A leveling bulb connects to the tube by a heavy rubber tube.

Among the advantages of this apparatus over the old

forms may be mentioned the following: It can easily be cleaned. The platinum spiral extending the full length of the tube insures complete combustion. This spiral can readily be removed for repairs in case of injury. The apparatus is convenient to handle and owing to its tall form connects with a Hempel pipette without the use of a stand.

The apparatus can be obtained from Messrs. E. H. Sargent & Co., Chicago. WILFRED W. SCOTT.

DETERMINATION OF INSOLUBLE PHOSPHORIC ACID.[1]

Ever since the organization of the Association of Official Agricultural Chemists the Official method for the determination of insoluble phosphoric acid has been confined to the one process; that is, digestion in neutral ammonium citrate for a definite length of time at a stated temperature. From time to time some slight modifications have been proposed, but in the main, the method remains practically the same as it was twenty-five years ago. One difficulty which has been experienced, is to make an ammonium citrate which is exactly neutral, owing to the indefinite action of the solution on different indicators. The "official" method prescribes corallin as the indicator to be used in testing the neutrality of the solution. Any one who has tried this indicator knows how unsatisfactory it is, and it is safe to say that there is not one chemist in ten who depends upon it for the final test. The optional method provides for first neutralizing with corallin as the indicator, and making the final test with cochineal after precipitating out the citric acid with calcium chloride. This procedure is also unsatisfactory, and as Dr. McCandless, referee of phosphoric acid for the A. O. A. C. for the past year, truly said: "If a chemist has succeeded in getting his solution neutral or practically so, he will almost certainly get his out of joint by attempting to make it exact with calcium chloride solution." The result is that different chemists employ different methods for standardizing the ammonium citrate solution, and hardly two solutions will be found of exactly the same neutrality. Instead of prescribing two methods which may give entirely different results the A. O. A. C. should prescribe one method which can be easily worked and would prove satisfactory to a majority of the chemists who are engaged in fertilizer work. Dr. McCandless favors making the solution neutral by analysis, and calculating the exact quantity of ammonia or citric acid to be added. A citrate solution which is neutral by analysis is distinctly alkaline by the ordinary indicator, and while it would be quite a departure from the Official method, it would at least insure a greater degree of uniformity than it is possible to obtain under the present methods. It is fortunate that a slight deviation from strict neutrality has no appreciable effect in the ordinary acidulated goods, but in cases of bone, tankage, etc., it is very important that the solution should be neutral.

There is another point that seems to have been overlooked in carrying out this method which causes quite wide variations in results by different analysts; that is, the manner of filtration after digesting with ammonium citrate. I have investigated the question to some extent, and find the following methods of filtration in use in different laboratories. Through asbestos in Hirsch funnel with filter pump; through asbestos on carbon filter with filter pump; through filter paper on Hirsch funnel with filter pump; through filter paper in Buchner funnel with filter pump; through filter paper with regular funnel and platinum cone using filter pump; through folded filters without filter pump.

[1] Paper read before the Division of Fertilizer Chemists at Baltimore, December 31, 1908.

The filter papers used in the above vary from very thin to dense slow filtering papers. Experiments which we have made by these different methods show that the results will vary on some samples of acid phosphate having a high percentage of insoluble from ½ per cent. to 1 per cent. and on such materials as ground bone, tankage, reduced phosphate, basic slag, etc., it is probable that there would be much larger variations.

The exact wording of the "official" method with reference to the filtration is as follows: "At the expiration of exactly thirty minutes from the time that the filter and residue are introduced remove the flask from the bath, and immediately filter the contents as rapidly as possible." Now if this were amended so as to specify the exact method of filtration and the kind of paper to be used, much of the confusion in results would be avoided. Taking everything into consideration, this method if properly executed, serves the purpose for which it was intended in a very satisfactory manner, and these few comments are presented with the hope that this division will take up the question and evolve a method which will not only be acceptable to the fertilizer chemists, but will be adopted by the Association of Official Agricultural Chemists. F. B. CARPENTER.

COUNCIL ON PHARMACY AND CHEMISTRY, REGULATIONS RELATIVE TO NEW AND NON-OFFICIAL REMEDIES.

The last meeting of this Council of the American Medical Association was devoted to the discussion of the revision of the rules, and rearrangement of the matter contained in the "New and Non-Official Remedies." It was decided that this book shall contain descriptions of the proprietary articles accepted by the Council and of such simple non-proprietary and unofficial substances as are of sufficient importance. It was decided that proprietary mixtures unless they show originality and a marked advance over similar products, shall not be included in the main body of the book, but when they conform to the rules, they shall be included in form of an appendix to the book.

Rule 5 was so amended as to require that the actual identity of the manufacturer of a product be furnished. The Council voted to interpret Rule 8 so that after January first, 1909, pharmaceutical preparations and mixtures will be admitted only under a pharmaceutical title which shall indicate the most potent ingredients. Arbitrary coined titles will not be recognized for pharmaceutical mixtures. It was also decided that no pharmaceutical mixture shall be accepted whose name indicates its therapeutic action or is suggestive of the names of diseases or pathologic conditions in which it is to be used. After January first, 1909, this rule is to be extended to simple articles.

The Council voted to condense Rules 9 and 10 to become Rule 9 and adopted a new Rule, No. 10, under which recognition will be refused to articles which, because of their unscientific composition, are useless or inimical to the best interests of the public or of the medical profession.

These rules represent a material progress made in the gradual elimination of deception and fraud which has been in practice, without restraint, for many years. During recent years, with the great influx of newer remedies, there has appeared in the European and American markets, a large number of preparations, so named and labeled as to suggest either their therapeutic action, or similarity to other established true synthetics. These preparations, being mechanical mixtures of well-known therapeutic agents, are therefore calculated to deceive the medical profession, and considering the persistence with which they are pushed, it is high time that concerted action be taken by chemists, physicians and pharmacists on both sides of the Atlantic, in order to control this nuisance.

V. COBLENTZ.

QUOTATIONS.

THE OXIDATION OF ATMOSPHERIC NITROGEN.

By DR. OTTO SCHNEIDER.

(Lecture delivered before the Verein Deutscher Chemiker, 1908. Authorized translation—Extracts.)

In the process of the Badische Anilin & Soda Fabrik, electric arcs produced by powerful currents and of a length never before attained are used. But these arcs burn very quietly, and special care is taken to displace them as little as possible by the motion of the air by causing the air to flow along the arc in the direction of its length. This way is so entirely different from the traditional one that there was no lack of dissenting voices who called in question the practical utility of our method, and curiously enough, by giving diametrically opposite reasons. Some said that this method of conducting the air did not allow it to come sufficiently in contact with the arc, while others claimed that it remained in contact too long.

Well, in the meantime we have demonstrated that our process can compete successfully with any other. The principle of the process consists, as we have already indicated, in conducting the gases to be acted upon along a quietly burning electric arc of great length, in surrounding, as it were, the electric arc with an advancing mantle of gas. The apparatus with which the operation is conducted is as simple as the principle itself. It consists essentially of a tube in the axis of which the electric arc is quietly burning surrounded by a mantle of the gases which are to be combined. The tube itself and the motion of the air in it must be so arranged that any one-sided motion in the direction of the arc is avoided as perfectly as possible, while it does no harm if the air comes from two opposite sources or is introduced towards the arc through a slit with equal pressure from all directions at once because this does not disturb the position of the arc.

Now, there is one kind of motion which satisfies this condition particularly well. For this reason we have used it almost exclusively in our method on a large scale. It enables us to obtain arcs of enormous length, which at the same time are so stable that they can burn for weeks without having to be relighted. This is a motion of the air which in spite of the greatest rapidity permits that portion of the column to remain at rest in which the arc is situated. This kind of motion is familiar to you all, it is the spiral or vortex motion. You all know with what devastating power cyclones visit certain regions of the earth with terrifying regularity. They move like a solid mass across the country for miles laying low everything before them. Nothing is able to withstand the impact of this whirling air and yet they carry in their centre a region of calm.

We have utilized this phenomenon. We generate such a vortex in miniature in our tubes and in its calm centre we maintain our electric arc. The particles of the air rush along the arc in a rapid screw-like motion and are combined in the desired way. In this way electric arcs of almost any desired length may be kept burning quietly.

The tube may be made of any material. We take for example an ordinary iron gas-pipe. An electrode insulated from the pipe is attached on the inside at one end and the air is introduced at this end. The insulated electrode is connected with one pole of a high tension current and the pipe itself with the other pole. The whirling motion of the air is produced in the simplest possible manner by tangential introduction. The arc is then lighted in any desired way. I will not mention the different ways in which this can be done, as they are well known to every electrician.

It is immaterial which way is chosen in our process, because, as we have already stated, the arc when once lighted can be maintained for weeks without relighting. In the simplest form the arc may be started by making the distance between the pipe and the electrode so small that it will be overcome by the tension of the interrupted circuit. As every electric arc must be provided with an inductive resistance which is indispensable to produce quiet burning and which is present in every ordinary alternating current arc lamp, the tension between the electrode and the pipe is diminished by a certain amount as soon as the arc is lighted and with this diminished tension the current will not jump across again as long as the arc continues to burn. If it should go out for any reason, a new arc will be formed of itself because of the renewed increase in the tension. With this method of forming the arc the air enters the tube below the electrode and pushes one end of the arc, which is quite short at first, rapidly before it along the wall of the pipe. As soon as stability is reached, which comes to pass so quickly that the eye is hardly able to follow the process, the result is an arc which burns quietly in the axis of the pipe, its end being far from the electrode attached to the centre. This end is at that point of the wall of the pipe where the gases have become so hot as to acquire sufficient conductivity for the current to jump across them. The location of this point depends entirely on the conditions adopted. Of course the place where the arc terminates must be cooled off by means of water or in some other suitable way.

The method of starting the arc which has just been described requires a very narrow space between the pipe and the electrode. A certain pressure is used to make the air which is introduced pass through the narrow space. This inconvenience is avoided by introducing the greater part of the air above the electrode, or by increasing the space, and producing in some way a brief temporary short circuit between the pipe and the electrode, as for example by means of a rod introduced from the outside, or an induction spark or a slender flame and the like. It does not matter because the arc when once lighted properly keeps on burning quietly, as has been stated, without going out. The tube may also be made of non conducting material, such as fire clay for example. In that case the arc must be

started by a temporary approach of the second electrode or by the use of a conductor along the wall of the tube to bridge over the space between the electrodes.

You see here three small furnaces with glass tubes constructed to illustrate the lecture. In two of these tubes there is placed a wire wound spirally and connected with the upper metallic post of the apparatus which forms the second electrode. The object of using the spiral form is to make the wire lie fimly against the wall of the tube. At the lower end this wire is separated by a very small space from the electrode situated in the axis of the tube, so that an arc may be formed there in consequence of the tension existing in the circuit. This apparatus illustrates the case where the tube is made of metal. We may imagine that the wire is all that is left of an original entire wall of metal. If the apparatus were entirely of metal you would not be able to see the rapid upward course of the electric arc. I now admit the air with a certain velocity through a tangential attachment below the spot where the electrode and the wire are separated by a short distance and connect the lower electrode with a high tension current. You will immediately see one end of the arc climb up along the wire and as a result an elongated arc burning quietly like a candle or a gas flame. And it is, in fact, a gas flame that you see, it is burning nitrogen. The arc proper, that is to say, that portion in which the electric current chiefly passes, is much slimmer than what you see—a fact which can be shown by passing a single gas, for example nitrogen alone, through the apparatus. The slight irregularity in the shape of the arc is due to the fact that the air flows through the tube with a simple screw motion. If the air were admitted through several openings or uniformly through the whole circumference, the arc would form a perfectly straight line. Please observe that the arc does not touch the wire while burning, but only when it is started.

In the other apparatus there is no wire inside the tube. Here I must start the arc by bridging the distance between the two electrodes by momentarily connecting them with a wire. The arcs in the small apparatus consume about 4 amperes at 3000 volts or in round numbers 16 h. p. of electric energy. You see the resulting product in the flasks of the apparatus in the form of a yellowish brown vapor.

As is well known, the first product in the electric arc is colorless nitrogen oxide which then oxidizes further to NO_2 on cooling in consequence of the excess of oxygen present. In maufacturing on a large scale these nitrous gases are first used for heating steam boilers and when they have been cooled in this way they are passed through percolating towers with water, where they are converted into nitric acid which is used to dissolve limestone. In this way a solution of calcium nitrate is obtained which is evaporated in a vacuum by means of steam. This lime saltpetre is equal to Chile saltpetre in every respect as a fertilizer and even superior to it for soils poor in lime.

After the details of our furnaces had been tested in the years 1905 to 1907 in Ludwigshafen, we started an experimental factory of 2000 h. p. last autumn in Christianssand, South Norway, in order to test our furnaces by long-continued operation. Three furnaces are now in continuous operation in Christianssand. The length of the flame is about 5 meters and their energy about 600 h. p. We have run one furnace temporarily with 700 kilowatts or approximately 1000 h. p. These enormous electric arcs are kept burning just as easily and surely as the much smaller ones I have shown you here. This is the more surprising when we consider that an alternating current of 50 periods is equalized in them, that is to say, that the current ceases 100 times per second when it passes zero and then flows through its long path again in the opposite direction without requiring the arc to be relighted. These manufacturing furnaces, to be sure, look rather different from the lecture apparatus exhibited here. In them the air is systematically heated by the hot discharge gases to about 500° C. before its entrance in the electrode pipe proper. The principle, however, is the same after all. To obtain a good result the pipes must have the right dimensions, the air must be supplied uniformly and the upper part must be well cooled. All this is easily accomplished in our furnaces, as you see. These furnaces are very durable. The only part subject to more rapid wear is the lower electrode and this we cool specially with water in our industrial furnaces. In its simplest form, as in the lecture apparatus before us, it may consist of an iron rod which may be moved forward for adjustment, but other materials may also be used for electrodes. Conductors of the second class, as for example zirkon oxide, may also be employed.

Our process differs from all other known methods by its excellent utilization of the electric energy and at the same time by yielding a gas of relatively high concentration which essentially facilitates absorption. The apparatus is extremely simple and cheap. There are no movable parts, expensive magnets or the like, and as the arc burns quietly the factor of electric efficiency is high.

It will not be long before saltpeter factories will spring up wherever circumstances permit. I suppose it is generally known that we have combined with the owners of the Birkeland-Eyde process in order to work together. For this purpose factories with 120,000 h. p. are in process of construction in Norway. It is true that the new industry is limited by the presence of very cheap sources of power, but for this very reason it is doing pioneer service by opening to industry regions which might have remained dormant for many decades if it had not been for the sudden demand for great quantities of cheap energy.

THE PRODUCTS OF THE BADISCHE ANILIN- AND SODA-FABRIK.

(From *The Badische Book*, 1908.)

The enormous progress and changes which have taken place in the course of the past century in industry and commerce, are due, to a great extent at least, to the utilization of the energy stored up in coal. * * * Chemical science and the art of the manufacturer have succeeded in producing from coal an unlimited series of valuable dyes, and by this meansh ave brought into existence a flourishing industry.

It is but little more than thirty years ago that dyers were entirely dependent upon the so-called natural coloring matter obtained from plants and animals, or prepared from minerals, from metals or from earths. The introduction of dyes derived from coal tar led to a complete change in the dyeing industry. * * * This brilliant success must be attributed

principally to the intimate connection between factory work and scientific investigation.

The history of the development of the coal-tar color industry is intimately associated with the history of the Badische Anilin- & Soda-Fabrik. At first this company only manufactured the few aniline dyes which were then known, such as Magenta, Aniline Blue, etc.; but in course of time a large number of the most important discoveries of science were utilized and the range of manufacture continually widened. * * *

In the manufacture of gas and coke from coal, tar is obtained as a by-product. From the tar, by distillation, benzene, toluene, xylene, naphthalene and anthracene are obtained, and these, together with gallic acid, a product of the vegetable kingdom, are used by the company as the initial materials for the production of dyes.

From the beginning, the company has worked upon the principle of itself producing all the materials used as reagents in working up and converting the initial materials into dyes. This results in the manufacture of so-called "heavy chemicals," the products of the acid and soda industries, *viz.*, sulphuric acid, sulphuric anhydride, hydrochloric acid, nitric acid, soda, chlorine, chromic acid, etc. For this purpose iron pyrites, salts, limestone, saltpeter, chrome ore, etc., are employed. The company can also claim to have enriched this branch of industry with a number of valuable achievements, especially by the method of the manufacture of sulphuric acid without lead chambers (1889), which later became of such epoch-making importance and caused a complete revolution in the sulphuric acid industry; the manufacture of liquid chlorine (1888), and recently by the industrial manufacture of stable solid sodium hydrosulphite, which is used for discharging and bleaching and also in the preparation of the indigo vat. Rongalite, which is employed in discharge printing, is derived from it.

The company has for a number of years past availed itself of the achievements of electro-chemistry in making chlorine and caustic soda by the electrolytic process.

The first important success of the Badische Anilin- & Soda-Fabrik in the manufacture of organic coloring matters was the commercial production of alizarine. In the year 1868 Graebe and Liebermann succeeded in preparing alizarine, the important coloring-matter of the madder root, from a hydrocarbon, anthracene, contained in coal-tar. The Badische Anilin- & Soda-Fabrik worked with the discoverers in order to formulate and establish a rational process for the commercial manufacture of this dye, and this object was achieved in the year 1869. By means of this process, artificial alizarine has since been manufactured. The production of this coloring-matter has increased enormously and has proven to be of very far-reaching importance to the industry.

The maufacture of alizarine soon resulted in the introduction of important derivatives therefrom; among these may be mentioned in the order of their importance: Alizarine Blue (1878), and especially the soluble form of the same dye, Alizarine Blue S (1882), Alizarine Green and Alizarine Indigo Blue (1888), Anthracene Blue (1891), Alizarine Orange (1875), and Alizarine Maroon (1885). Closely connected with these colors produced from anthracene are some derivatives of gallic acid, namely, Galleine Coeruleine (1878), Anthracene Brown (1880), and Galloflavine (1886), and in the year 1887 the series of mordant dyeing coloring agents was rounded off by the manufacture and introduction of the fastest black coloring-matter—Alizarine Black, which is a derivative of naphthalene. * * *

A new important group of anthracene colors, whose dyeing properties indicate them to be acid-coloring agents of the anthraquinone series and which are distinguished by their eminent fastness, was introduced a few years ago. To these belong Anthraquinone Blue (1901), Cyananthrol (1902), Anthraquinone Violet (1902), Anthraquinone Green (1904). * * *

The Eosines were discovered in the year 1874 and were the first dyes of the resorcine class, to which belong also the Rhodamine dyes discovered in 1887. Methylene Blue, discovered in 1877, is one of the most valuable dyes for cotton. In the same year Acid Magenta, in 1878 Naphthol Yellow S, and in 1879 the first Acid Green, Light Green S, were discovered, and they are to this day absolutely essential in wool dyeing.

In the year 1883 the industry was greatly enriched by the introduction of coloring-matter syntheses effected with the aid of phosgene. The research work in the new region thus opened up led at once to the discovery and manufacture of Crystal Violet, Victoria Blue, Acid Violet, Alkaline Violet and Wool Green, and especially of the most important dye, Auramine, which is largely used in dyeing cotton, paper and leather.

In the Induline class of dyes Acetine Blue has been manufactured since 1886 and has attained importance in calico printing, while Azocarmine, discovered in 1888, is an important color for dyeing wool.

The Badische Anilin- & Soda-Fabrik also took a leading part in opening up the great field of azo-coloring agents. Among the number of important dyes of this class discovered by its chemists, are especially to be mentioned Fast Red (1878) and Blue-Black (1882), the first black azo-dye. Brilliant Black may be regarded as a successor of this latter, as may also the more modern Palatine Black and Palatine Chrome Black, which are used in the place of logwood in dyeing wool black.

In the year 1891, the Badische Anilin- & Soda-Fabrik brought into commerce Indoine Blue, an exceedingly valuable product for dyeing cotton, and among the further successful discoveries of the company a number of important cotton dyes must be mentioned, in particular Nitrosamine Red (1894), several substantive azo-dyes: Cotton Yellow, Carbazol Yellow, Pyramine Orange, the Oxamine dyes, etc.—and the new class of sulphur dyes—Fast Black, Kyrogene Brown and Anthraquinone Black—all of which possess a high degree of fastness. Further, the introduction in 1895 of Rheonine, a valuable yellow dye for leather, deserves mention, as does also Lithol Red (1900), an azo-coloring matter which has become of the greatest importance in the lake-color industry.

Quite a special interest both on the practical and on the scientific side, attaches to the extremely fast coloring agents of the Indanthrene class introduced in 1901: Indanthrene Blue, Indanthrene Yellow (Flavanthrene), Indanthrene Gray (Melanthrene), Indanthrene Maroon (Fuscanthrene), to which have more recently been added the following products: Indanthrene Dark Blue BT and BO (Cyananthrene 1904, Violanthrene 1905), Indanthrene Green (Viridanthrene 1906), and Indanthrene Violet (1907), all derivatives of

Benzanthrone; Indanthrene Bordeaux (1908) and Indanthrene Red G and R (1908), derivatives of Dianthraquinonylamin; the derivatives of Methylanthraquinone-anthraflavone (1907), Indanthrene Orange-gold (Pyranthrene 1908), and further Indanthrene Olive (Olivanthrene 1906), Indanthrene Orange (Fulvanthrene 1908), Indanthrene Brown (Rufanthrene 1907) and Indanthrene Copper (1908).

The oldest and most important of the coloring agents obtained from the vegetable kingdom are Alizarine and Indigo. The Badische Anilin- & Soda-Fabrik having at an early date succeeded, as already mentioned, in producing the former of these commercially from anthracene. In 1881 Baeyer had solved scientifically the problem of preparing Indigo synthetically, and in 1890 Heumann succeeded in discovering a new solution of this important question. Working together with these eminent scientists, the company endeavored to make these important discoveries commercially useful, and after persevering continuously for many years and devoting to the matter costly work without stint, its labors were finally rewarded with success. The great object is achieved—indigo can be produced from coal-tar artificially in a manner that renders it capable of competing with the product obtained from the indigo plant, and since July, 1897, the Badische Anilin- & Soda-Fabrik has placed synthetic indigo on the market under the name of "Indigo Pure B. A. S. F." This marked the beginning of a new epoch in the history of the coal-tar color industry, for the manufacture of this new product constitutes an addition of quite eminent importance to its field of operations.

The substitution of artificial dyes used for ages in the dyeing industry is the goal for which the coal-tar industry has consistently striven to attain. The economic importance of this is obvious: First, the building up of a great industry, and second, the releasing of vast areas for other and more profitable purposes than the cultivation of natural dyes. To-day many million kilograms of artificial alizarine are manufactured annually, and the use of Madder has almost entirely ceased. Cochineal was formerly used in large quantities, in round figures about 600,000 kilograms were used in Germany in the year 1872, but in 1907 the quantity used was only 71,000 kilograms. Archil has had to yield to the red azo-colors and to azo-carmine. Curcuma has been displaced by fast yellow, auramine and others, and tartrazine has replaced flavine. A large proportion of logwood hitherto employed has been replaced by black azo-dyes and alizarine black, and indeed the alizarine dyes generally threaten the dye-woods, and finally, even vegetable indigo has been met by a victorious competitor in synthetic indigo. The introduction of the latter was a complete success. Founded on an installation on the largest scale, and carried on with the express intention of driving the natural product entirely from the field, the manufacture of synthetic indigo has now reached enormous proportions and is continually increasing. Corresponding to the increase in the production of synthetic indigo, that of the natural product is diminishing so that the cultivation of plant indigo, which even in 1897 showed a production of five to six million kilograms of a value of from sixty to eighty million marks, has sunk to about one-fifth. For instance, the Calcutta crop amounted in 1896 to 158,923 maunds, and 1906 to only 33,360 maunds. In 1898 there were 122 indigo plantations in Java, where there are now only 28, and the crop has sunk from 12,580 chests in that year to 2,295 in 1907. The value of the plant indigo imported into Germany in 1897 was about 12,700,000 marks, but in 1907 only 1,083,000 marks, while on the other hand the export of synthetic indigo from Germany reached in 1907 the value of 42,582,000 marks.

The issue of the struggle between the artificial and the natural product is no longer doubtful, plant indigo will in no long time share the fate of Madder, and practically disappear from commerce. * * *

The annual production in Germany of artificial organic coloring-matters represents a value of 250,000,000 marks.

The Badische Anilin- & Soda-Fabrik has recently turned its attention to one of the most important problems of modern chemistry, namely, the utilization of the nitrogen of the air. The company has succeeded, by means of an original process, in burning the nitrogen of the air in an electric arc flame, and is now about to carry out its process on the largest scale in Norway, utilizing the enormous water power which that country has at its disposal. Agriculture needs enormous quantities of saltpetre, the most important plant manure, and the demand grows from year to year so that within a short period the saltpetre deposits of Chili, up to now the sole source of this product, will be exhausted. The yearly production of Chili saltpetre amounts to 1,800,000 tons, of which the German agriculture absorbs about 500,000 tons. From these figures some idea can be obtained of the importance of the future of this industry, which is destined to supply the world's demand of saltpetre.

BOOK REVIEWS AND NOTICES.

Principles and Practice of Agricultural Analysis. Second edition, revised and enlarged. Vol. II. Fertilizers and Insecticides. By HARVEY W. WILEY, A.M., Ph.D. 8vo, 680 pp. Illustrated. Easton, Pa.: Chemical Publishing Co. 1908. Price, $4.50.

This is the standard work on agricultural analysis in the English language and is so well and favorably known in the first edition that it is hardly necessary to comment in general terms on the second. The principal addition to the present volume is that portion of the work devoted to insecticides and fungicides, amounting to some twenty-eight pages. However, the book has been in large part rewritten and new matter has been added wherever it was necessary to bring the work down to date. For instance, numerous pages have been added in Part I, devoted to phosphates and phosphatic fertilizers, under the headings of definitions, sampling and preliminary treatment, drying samples of fertilizer, mineral phosphates, direct weighing of the yellow precipitate, etc. Part II is devoted to nitrogen in fertilizers and here again extensive additions have been made so that this part is more than twice as large as in the first edition. Again, in Part III, devoted to potash in fertilizers, many new pages have been added and several new illustrations. The first edition of the work numbered 332 pages. The second numbers 680, and is correspondingly complete and up-to-date. Not the least interesting pages are those devoted to the utilization of the nitrogen in the air as a fertilizing material, which includes the fixation by soil bacteria, in the form of cyanamid, and as nitric acid or the nitrate

after oxidation to nitric oxide in the electric arc. There is so much new matter in the second edition that even fertilizer chemists who already possess the first may well add the second to their library. We shall look forward with interest to the publication of the third volume of this important work. W. D. RICHARDSON.

The Mechanical Appliances of the Chemical and Metallurgical Industries. By OSKAR NAGEL, Ph.D. 8vo. pp. vii + 307. New York. Published by the author. 1908. Price, $2.00 net.

There has been a great need for just such a work as Dr. Nagel's for some time, and on the whole, the author has satisfied this want ably and well. As an aid to the professor, college student, the works chemist or works manager, the book will be found of service, while the engineer himself may look through the work with profit. Here are gathered together in systematic form the mechanical appliances of the chemical industries and the organization alone of the great mass of material in this field and the elimination of all but the essentials is a worthy task. The instruction of the young chemist in college in the ways and means of applying his science to the practical exigencies of chemical manufacture is difficult. Dr. Nagel's book will certainly help greatly in this respect. The book is composed of fifteen chapters and is copiously illustrated with well-selected cuts.

Chemical Reagents: Their Purity and Tests. By E. MERCK. Translated by Henry Schenck. 8vo. pp. vi + 250. New York: D. Van Nostrand Company. 1907. Price, $1.50 net.

This work based on the previous one of Dr. Krauch, is of great service to the chemical profession generally and to all who have occasion to use pure chemicals. Probably no other work has had so great an influence in developing manufacturing standards for pure chemicals. The day of the C. P. chemical is past. The day of the analyzed chemical is at hand, and we must admit that in this revolution the works of Krauch and Merck have had a preëminent place. The book can be added to the library of any chemical laboratory with advantage.

Modern Power Gas Producer. By HORACE ALLEN. 12mo. pp. vii + 326. New York: D. Van Nostrand Company. 1908. Price, $2.50 net.

The literature on producer gas, gas producers and gas as a source of power, is increasing monthly, but hardly rapidly enough to keep pace with engineering progress along these lines. The present work is a valuable addition to those that have gone before, and presents in compact and useful form the essentials of gas production and utilization. There are 22 chapters, covering the different varieties of gas, the gasification of fuel, several chapters on gas producers and the application of gas to internal combustion engines. The illustrations are good and the work should prove useful to chemists and chemical engineers.

Chemiker-Kalender, 1909. By DR. RUDOLPH BIEDERMANN. Part I, cloth, pp. 384 Part II, paper, pp. 562. Berlin: Julius Springer. 1909. Price, 4 marks.

Again the chemists of the world extend their annual greeting to the Chemiker-Kalender (now in its thirtieth year) which has served them so long and so usefully. It is, of course, unnecessary to make any extensive comments on the nature and contents of a book so widely used and favorably known as this one. Four pages have been added to Part I, and six pages to Part II, for the current year. The print, paper and general make-up has not been altered. If we could make a suggestion to the publishers, we should like to ask whether or not the two parts could not be bound in one volume with advantage.

Laboratory Experiments in Metallurgy. By ALBERT SAUVEUR and H. N. BOYLSTON. Small 4to. pp. 73. Cambridge, Mass. Published by the authors. 1908. Price, $1.25 net.

It is said in the preface that this work is intended primarily for the use of students at Harvard University, who take the course in general metallurgy and metallurgy of iron and steel. The intention is also announced of extending the number of experiments, in the desire to make the book more comprehensive, in future editions. The work is divided into two parts: Part I, General Metallurgy, 30 pages; Part II, Metallurgy of Iron and Steel, 68 pages. There are ten tables and seventeen illustrations. The work is so arranged that the student can easily make notes of his experiments, being interleaved. On the whole, the book is a needed one and serves its purpose well. A number of minor criticisms might be suggested. For instance, under calorimetry, the Parr calorimeter is used in one experiment, but no mention is made of the oxygen-bomb calorimeter. The Parr calorimeter is certainly worthy a place in the book but not to the exclusion of the oxygen-bomb. Among the tables is a copyrighted one by Riehlé Bros. It would seem that the size of the type used in the tables could be increased with advantage, and the size of type in which the name of the firm is printed, could be reduced, also with advantage. Several good cooling curves for iron and steel are given and it would seem that the descriptive matter covering these experiments might be extended. No doubt it is intended to do this in the lectures accompanying the course. As stated above, on the whole, the book serves a very useful purpose and will be found valuable by teachers of metallurgy.

Laboratory Notes on Industrial Water Analysis. By ELLEN H. RICHARDS. 8vo. 49 pp. New York: John Wiley & Sons. 1908. Price, 50 cents, net.

Apparently this work is the outgrowth of teaching experience and designed for a particular class of students. It adds another to the list of many useful books from the pen of the same author. While the previous works dealt largely with sanitary science, the present one deals quite as largely with the engineering side of the subject. The special methods of analysis are principally considered and attention given only in lesser degree to general methods of analysis. On the whole, the book is good and useful and, within its scope, few criticisms are to be made. One point to be noticed is the occasional use of language which is not exactly scientific, or is at least unusual. For instance, on page 14, "incrustants *par excellence*." Definite expressions are in use among chemists for definite things and should be adhered to as much as possible. Among the tables, it would seem that, even though no great changes have been

made, a later International Atomic Weight table than that for 1905 might be given. The author says a good word for the right method of reporting when she deprecates the waste of time spent on elaborate calculations of water analysis. The method of the U. S. Geological Survey of reporting constituents as ions is certainly to be approved and in any case the actual analytical data, either as ions or oxides, should be given, along with the possible combinations reported. As the author states, the public soon learns to take results and interpret them as given. This is true and it is unfortunate that in so many industrial analyses at the present time, the data is not given while the hypothetical combinations are.

Die Fabrikation von Leim und Gelatine. By DR. LUDWIG THIELE. 16mo. pp. 158. Hannover: Dr. Max Janecke. 1907. Price, $—.

This little book is divided into nine chapters and covers in a very excellent manner, considering the limited amount of space, the manufacture of glue and gelatine under the following heads: Composition and Purposes of Glue and Gelatine; Raw Materials; Manufacture of Bone Glue; Trade Names and Uses of Various Glues; Preliminary Treatment of the Raw Material for Hide Glue and Gelatine; Gelatine; Fish Glue; The Testing of Glue; Plant for Glue Manufacture. Comprehensive works on the manufacture of glue are almost an unknown quantity. Most are of the briefer sort and too few are up-to-date. Among the briefer texts, this little book of Dr. Thiele's should find an acceptable place.

Les densities des solutions sucrées à Différentes temperatures. By D. SIDERSKY. In French and German. H. Dunod and E. Pinat, Paris. Friedr. Vieweg & Sohn, Brunswick. 1908. 48 pages with tables. Price unbound, 3.50 francs.

The importance of the determination of specific gravity in the chemical control of sugar factories has given rise in past years to a multiplicity of tables for the estimation of total solids. The various tables of Balling-Brix, Gerlach, Scheibler, and others when compared show, however, certain differences, a circumstance due partly as to whether the weight of water at 15° or 17°.5 was used as a basis and partly also to errors in observation. The efforts of the author in the present work have been directed towards evolving some order out of the chaotic condition of the literature upon this subject. As a basis of calculation he has used Plato's specific gravity table of sugar solutions adopted by the Kaiserliche Normal-Eichungskommission and now considered to be the most accurate. The tables are divided into two parts: the first part for dilute sugar solutions (0° to 5° Brix) gives the actual and relative density $D\frac{t^\circ}{4^\circ}$ and $D\frac{t^\circ}{15^\circ}$ to the fifth decimal with the corresponding percentages of sugar for each degree between 10° and 30°; the second part for more concentrated sugar solutions (5° to 30° Brix) gives the $D\frac{t^\circ}{4^\circ}$ and $D\frac{t^\circ}{15^\circ}$ to the fourth decimal with the corresponding percentages of sugar by both weight and volume at 10°, 15°, 20°, 25° and 30°.

For sugar solutions of density less than 1.13, the new specific gravity tables of Sidersky are unquestionably the most complete of their kind. Their practical value in sugar house work is, however, somewhat limited, being confined to sugar solutions below 30° Brix; for the sake of uniformity, therefore, many sugar chemists will no doubt prefer to continue using the older tables which have a range of from 0° to 95° Brix. It is to be hoped that the author may enlarge his tables so that they can be applied to syrups and sugar solutions of higher density. The text accompanying the tables is printed on opposite pages in French and German, an arrangement of great advantage to such as are familiar with but one of these languages. C. A. BROWNE.

"Effects of Formaldehyde upon Digestion and Health," Bureau of Chemistry, Circular No. 42.—In this circular, the Bureau, after describing the experiments, gives the following statement: "The final conclusion, therefore, is that the addition of formaldehyde to foods tends to derange metabolism, disturb the normal functions, and produce irritation and undue stimulation of the secretory activities, and therefore it is never justifiable."

The Decennial Index (1896–1905) of the *Journal of the Society of Chemical Industry* is now ready, price 11 s. ($2.75), and may be had by sending money order for the amount, payable to the Society of Chemical Industry, to Thomas Tyrer, Stirling Chemical Works, Stratford, London, E. The Collective Index (1881–1895) may be had at the same price.

The Bulletin of the Bureau of Standards, Volume V, No. 2, contains the following articles: Selective Radiation from Various Solids—W. W. Coblentz; Remarks on the Quartz Compensating Polariscope with Adjustable Sensibility—Frederick Bates; Methods of Obtaining Cooling Curves—George K. Burgess; Note on the Approximate Values of Bessel's Functions for Large Arguments—Louis Cohen; The Influence of Terminal Apparatus on Telephonic Transmission—Louis Cohen; The Principles Involved in the Selection and Definition of the Fundamental Electrical Units to be Proposed for International Adoption—F. A. Wolff; The Luminous Equivalent of Radiation—P. G. Nutting; The Temperature Formula of the Weston Standard Cell—F. A. Wolff.

Merck & Company have issued a pamphlet of eighty pages entitled "Prices and Uses of Tested Reagents, 1909." This work is a priced catalogue of Merck's tested reagents and contains under each item a list of tests to which the reagent has been subjected. The tests are those described in greater detail in "Chemical Reagents: Their Purity and Tests" published in 1907 by D. Van Nostrand Co., of New York, the volume which replaced Krauch's "Chemical Reagents." The booklet is useful to chemists and may be had by addressing Merck & Company, New York.

The Semi-Annual Report of Schimmel & Company, for November, 1908, contains an interesting article on Japanese Peppermint Oil, by Naojiro Inouye, of Harima, Japan,

from the laboratory of Prof. Edward Kremers, Madison, Wisconsin.

The Crane Company, Chicago, has issued an octavo pamphlet of 24 pages entitled "The Effect of Superheated Steam on Valves and Fittings" and written by the technical force of the company. This is timely and valuable. The use of superheated steam in the chemical industries and in engineering practice generally is greatly on the increase, whereas knowledge not only of its properties but of its effects, is inadequate to meet the situation. Under these circumstances, any contribution on the subject is to be welcomed. Following the introductory article which covers the effect of superheated steam on cast iron, on cast steel, on valve construction, on valve seats and stems, and on copper alloys (the effects of temperature from 70° to 950° F. upon the tensile strength of various alloys), there are a number of articles all bearing on the general subject reprinted from the *Valve World* for 1908.

Messrs. Schimmel & Company, the large essential oil distillers of Miltitz, near Leipzig, Germany, have issued a small and interesting volume on the subject of their plant and products. We note that the firm was founded in the year 1829 and erected its present plant in 1900. It is situated five miles from the center of the city of Leipzig, the total area owned by the firm being three hundred acres. The divisions of the book and subjects treated are: Power Plant, Main Factory, Chemical Department, Serum Department, Branch Distillery at Barrême, and Institutions for Social Welfare. The book is well illustrated and printed.

The Badische book, issued by the Badische Company, American representatives of the Badische Anilin & Soda-Fabrik, and distributed privately, is one of the best examples of book-making which has come to our attention from a manufacturing firm. It is bound and printed in excellent taste and contains a great deal of most instructive matter in regard to the works and products of the Company and its institutions for the benefit of its workmen. In another place we have quoted from the book, matter of considerable historical importance to chemical industry, and we note in passing that the products of the Company comprise the entire range of artificial organic coloring matters and all the intermediate and other products used in its manufacturing operations, including sulphuric acid, sulphuric anhydride, hydrochloric acid, soda, nitric acid, liquid chlorine, etc.; that the Company employs 217 manufacturing and research chemists, 142 civil engineers and 918 officials in the commercial department, besides 8000 workmen. The main plant of the Company is situated in Ludwigshafen on the Rhine. To the chemical engineer the name of the Badische will always recall with pleasure the splendid work of Rudolph Knietsch on liquid chlorine and sulphuric anhydride, as well as on many other chemical products.

Among the recent efforts by manufacturers to establish and maintain uniform methods of analysis, we note one in the form of a 12mo pamphlet issued by the laboratories of the Pfister and Vogel Leather Company, of Milwaukee, under the direction of Dr. Louis E. Levi, chief chemist, and Carl V. Manuel, chemist in charge. The book numbers 29 pages, is well printed and put together, is interleaved for notes and contains a large number of methods. We note that the acetine method is used for glycerine. A large number of practical and skilful chemists have found this method uncertain and unreliable and prefer Hehner's bichromate method.

NEW BOOKS.

Praktischer Tührer durch den Zeugdruck. By AUG. AXMACHER. Hannover: Dr. Max Jänecke. 1908. Price, geh. M. 6.60; geb. M. 7.40.

The Brewers' Analyst. By R. D. BAILEY. 8vo. Cloth. Ill. x+423 pp. New York: D. Van Nostrand Co. Price, $5.00

Chapters on Paper Making. By CLAYTON BEADLE. Vol. V. Concerning the theory and practice of beating. London: Crosby, Lockwood, and Son. 1908. Price, 5 s., net.

Analytische Chemie für Apotheker. By H. BECKURTS. Zweite neubearb. Aufl. mit 1 farbigen Tafel u. 96 abb. im Text. Stuttgart: F. Enke, 1908. Price, M. 11.60.

Chemiker-Kalender 1909. By R. BIEDERMAN. Ein Hilfsbuch für Chemiker, Physiker, Mineralogen, Industrielle, Pharmazeuten, Hüttenmänner usw. 30 Jahrung. Berlin: Verlag von Julius Springer. 1908. 1 Teil geb. in Leinwand-11 Teil. Price, geh. M. 4; in Leder, M. 4.50.

The Chemical Analysis of Iron. By A. A. BLAIR. Seventh edition. 8vo. Cloth. Ill. xix+334 pp. Philadelphia: J. B. Lippincott Co. 1908.

The Structure of the Wool Fiber, and Its Relation to the Use of Wool for Technical Purposes. By F. H. BOWMAN. New York: Macmillan & Co. 1908. Price, $2.25.

Le Parfum chez la Plante. By EUG. CHARABOT ET C. L. GATIN. Paris: Octave Doin. 1908. Price, 5 fr.

Chemisches Praktikum für Studierende der Naturwissenschaften. By MAX DITTRICH.

Die neuren Ansichten über die Erdöls. By C. ENGLER. Berlin: Verlag für Fachliteratur. W. 30.

Laboratoriumsbuch für Tinktorialchemiker, coloristen, Ingenieure, u. techn. Reisende in Färbereien, Druckereien, Farben-, Lack-, u. Papierfabriken. F. ERBAU. Mit 18 Abbild. i. Text. Halle a/S.: W. Knapp, 1908. Price, M. 2.50.

Fischer's Taschenbuch für Feuerungstechniker. By F. FISCHER. Anleitung zur Untersuchung und Beurteilung von Brennstoffen und Feuerungsanlagen. Leipzig: Verlag von Alfred Kröner. 1909. 6 neubearb. Aufl. M. 3.

Untersuchung und Nachweis organischer Farbestoffe auf spectroskopischen Wege. By J. FORMANEK. Zweite vollständig umgearb. und vermehrte Auflage. Erster

Theil. Berlin: Verlag v. Julius Springer. 1908. Price, M. 12.

Utilization of Wood Waste by Distillation. By W. B. HARPER. 4to. Cloth. Ill. 156 pp. New York: D. Van Nostrand Co. Price, $3.00.

The Mineral Industry. By W. R. INGALLS. 8vo. Cloth. Ill. xx+1,127 pp. Price, $10.00. New York: Hill Publishing Co. 1908.

Technologie der Gewebe-appretur. By BERNARD KOZLIK. Mit 161 in den Text gedruckten Figuren. Berlin: Julius Springer.

Technische Anwendung der physikalischen Chemie. By ARNDT KURT. iv+304 s. 55 Abbild. im Text. Berlin: Verlag von Meyer und Müller. Price, geb. M 8.

Technical Methods of Chemical Analysis. By GEORGE LUNGE, ED. English translation edited by Chas. A. Keane and others. Vol. I, Parts I and II. London: Gurney and Jackson. 1908. Price, 52 s. 6 d. net.

Technical Chemists' Handbook: Tables and Methods of Analysis for Manufacturers of Inorganic Chemical Products. By GEORGE LUNGE. London: Gurney and Jackson. 1908. Price, 10 s 6 d.

The Design and Equipment of Small Chemical Laboratories. By R. K. MEADE. Ill. 8vo. Cloth. Price, $2.00. iii+136 pp. Chicago: The Chemical Engineer Publishing Co. 1908.

Meat Extracts and Similar Preparations, Including Studies of the Methods of Analysis Employed. U. S. Dept. of Agriculture, Bureau of Chemistry, Bull. 114. Washington: Govt. Printing Office. 1908.

Der Dampf in der chemischen Technik. W. MOMBER. Halle a/S: Verlag von Wilhelm Knapp. 1908. 104 s. 26 fig. im Text. Price, geh. M. 3.60.

The Chemistry of Essential Oils and Artificial Perfumes. By E. J. PARRY. Second Edition, rev. and enl. London: Scott, Greenwood, and Son. 1908. 13 s.

Cement Laboratory Manual. By L. A. WATERBURY. 12mo. Cloth. Ill. vii +122 pp. New York: John Wiley and Sons. Price, $1.00.

Hevea Brasileinsis or Para Rubber. Its Botany, Cultivation, Chemistry, and Diseases. HERBERT WRIGHT. Third Edition. London: McLaren & Sons. 1908. Price, 10 s net.

Principles and Practice of Agricultural Analysis. H. W. WILEY. Vol. II, 2nd Edition, Rewritten, 8vo. Cloth. 68 pp. Easton: Chemical Publishing Co. Price, $4.50.

Royal Botanic Gardens, Kew. By W. J. BEAN. Historical and descriptive; with intro., by Sir W. Thiselton Dyer; ill with 20 reproductions in color from paintings by H. A. Oliver and 41 reproductions from photographs. New York: Cassell. Price, $7.50 net.

Electro-Metallurgy. J. B. C. KERSHAW. New York: D. Van Nostrand Co. Ill. (Westminster ser.). Cloth. Price, $2.00 net.

Laboratory Guide of Industrial Chemistry. ALLEN ROGERS. New York: D. Van Nostrand Co. 9 + 15 pp. Ill., tables, diagrams, plates. 8vo.. Cloth. Price, $1.50.

Glass Manufacture. WALTER ROSENHAIN. New York: D. Van Nostrand Co. 264 pp. Ill. 8vo. (Westminster ser.). Cloth. Price, $2.00.

SCIENTIFIC SOCIETIES.

THIRTY-NINTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The thirty-ninth general meeting of the American Chemical Society was held at Baltimore, Maryland, December 29th to January 2nd, inclusive. The meeting was the largest and most enthusiastic in the history of the Society. There were about four hundred members registered. In other words, ten per cent. of the total membership of the Society was in attendance.

Tuesday, December 29th was devoted to general addresses. In the morning, Messrs. A. D. Little, G. N. Lewis and C. H. Herty read addresses, which were followed by F. W. Clarke with a report of the International Committee on Atomic Weights. In the afternoon there was a meeting, largely attended, of the Section of Chemical Education, and after an address by the Chairman, Dr. H. P. Talbot, and an announcement by Dr. H. W. Wiley on the International Congress of Applied Chemistry to be held in London, May 27 to June 2, 1909, three addresses were read: Wm. H. Nichols, on "The Efficiency and Deficiencies of the College-trained Chemist when Tested in the Technical Field;" Louis M. Dennis, "To What Extent Should College Training Confer Practical Efficiency along Technical Lines?" and by Wm. McMurtrie, on "The Attitude of Technical Institutions to Post-graduate Study." A general discussion followed, which was participated in by Dr. Leo Baekeland, Dr. W. R. Whitney, Dr. H. W. Wiley, Prof. Louis Kahlenberg, Dr. C. B. Dudley, Dr. L. P. Kinnicutt and others.

This was the first meeting of the Section of Chemical Education and the interest and enthusiasm aroused indicate a successful future for this branch of the Society.

On Tuesday evening, at 8.00 o'clock, a complimentary smoker was given at the Hotel Belvedere, preceded by a very interesting talk illustrated with lantern slides by Wm. Simon, on the "Lumière Process of Color Photography." Upwards of three hundred persons attended the smoker, and the good fellowship which prevailed was unbounded.

On Wednesday morning there were meetings of the Agricultural and Food Section, the Biological Section, the Division of Industrial Chemists and Chemical Engineers, the Inorganic Section, the Organic Section, the Pharmaceutical Section and the Physical Section. In the afternoon there were excursions to the Naval Academy at Annapolis, to Sharpe & Dohme's factory and to the Baltimore breweries. In the evening at 8.00 P.M., the President of the Society, Prof. M. T. Bogert, delivered his annual address, on the subject "The Function of Chemistry in the Conservation of our Natural Resources."

On Thursday morning there was a general business meeting of the Society, followed by addresses by H. J. Wheeler, on "The Future of Agricultural Chemistry;" S. F. Acree, on "The Quantitative Study of Organic Reactions;" and Edward Kremers, on "The Classification of Carbon Compounds." Following the general session, the Divisions and Sections met and continued their programs. At 4.00 P.M. there was a meeting of Associate Editors and Abstractors of Chemical Abstracts, and at 5.00 P.M. a meeting of the Board of Editors of the *Journal of Industrial and Engineering Chemistry*. In the evening at 8.00 P.M. the subscription dinner at the Belvedere Hotel was attended by about three hundred members and guests, and was one of the most enjoyable events of the meeting.

On Friday morning, January 1st, there were adjourned meetings of the Sections and Divisions, and in the afternoon an excursion to the plant of the Maryland Steel Company at Sparrow's Point. On Saturday, January 2nd, there was an excursion to Washington to visit the Bureau of Standards and the Geophysical laboratory.

Possibly the most significant event in connection with this meeting of the Society was the granting by the Council of authority to establish several Divisions. This is in line with the policy which has been developed during the past two years. Authority was granted for the establishment of a Division of Agricultural and Food Chemists, a Division of Physical and Inorganic Chemists, a Division of Organic Chemists and a Division of Fertilizer Chemists. Any member of the Society is privileged to register in one or more of these Divisions and in this way affiliate himself with the particular branch or branches of the science in which his interests chiefly lie. With the Division of Industrial Chemists and Chemical Engineers, which was organized in the summer of 1908 at New Haven, the Society now has five Divisions, and it is likely that more will follow soon.

The following officers were elected: *President*, Dr. W. R. Whitney; *Secretary*, Chas. L. Parsons; *Editors*, W. A. Noyes and W. D. Richardson; *Treasurer*, Dr. A. P. Hallock; *Librarian*, Dr. E. G. Love; *Directors*, T. J. Parker and M. T. Bogert; *Councilors-at-Large*, Dr. W. Lash Miller, Chas. H. Herty and W. H. Walker.

It was decided to hold the next meeting of the Society at Detroit during the coming summer, the date to be fixed by the President and Secretary.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The Division of Industrial Chemists and Chemical Engineers held its second semi-annual meeting at Baltimore, in connection with the general meeting of the American Chemical Society. There were in attendance about seventy-five members, although more than this number have registered in the Division and the number is constantly increasing. The meeting was called to order by the Chairman, Dr. A. D. Little, of Boston, and the following papers were read: Walter O. Snelling, The Munroe Crucible; Percy H. Walker and H. A. Whitman, Rapid Analysis of Babbit Metal; Chas. H. Herty and W. S. Dickson, The Unsaponifiable Matter in the Oleo-Resins of Conifers; Allerton S. Cushman, Acceleration Tests of the Resistance to Corrosion of Iron and Steel; David W. Day, The Changes in Crude Petroleum Effected by Diffusion through Clay; George Auchy, Further Remarks on Vanadium and its Estimation; Paul N. Clancy, Iron from a Chemical and Commercial Standpoint; C. H. Ehrenfeld, An Unusual Incrustation on Generator Coils; H. J. Skinner, The Purchase of Material on Specification; F. A. Olmstead, Some Industrial Applications of the Ives Colorimeter; C. F. Woods, Factors Determining the Efficiency of Trolley Wires; E. B. Boughton, The Iodine Number and Some Other Values for China Wood Oil; E. G. Bailey, Accuracy in Sampling Coal; Chas. E. Munroe, The Commercial Manufacture of Amorphous Calcium Phosphide and The Distribution of Nitrate of Soda in the U. S.; L. A. Olney, Standard Methods for Determining and Recording the Relative Permanency or Resistance of Coloring Matters to the Common Color-destroying Agencies; A. G. Stillwell, Standardization of Methods for Commercial Analysis of Fats, Greases, etc., and Adoption of Rational Nomenclature for Same; Theodore Whittlesey, Guayule and Guayule Rubber; Arthur Lowenstein, The Rapid Determination of Moisture in Commercial Products of a Viscous or Semi-solid Consistency; C. F. Mabery, Lubrication and Lubricants; W. H. Walker, A Method for Testing the Continuity of Tin Plate.

Among the most interesting papers were those by Mr. E. G. Bailey, on "Accuracy in Sampling of Coal," and Wm. H. Walker, on "A Method for Testing the Continuity of Tin Plate," both of which will be published in this Journal at a later date.

Mr. Bailey called attention to the principal reasons for error in determining coal values by sample, and showed the reason why several so-called samples from the same car might vary greatly upon final analysis. Mr. Bailey's paper was illustrated by a series of elaborate charts which showed the factors of error.

Dr. Walker's paper called attention to the so-called pin-holes in the surface of tin plate and showed how he determined their exact location by flowing a gelatin solution of potassium ferricyanide over the plate. After a short interval, a blue spot appearing in the jelly located the pin-hole, and if it was desired to examine the pin-hole further, a circular punch stamp around the spot would locate it after the jelly was dissolved off.

Mr. T. A. Olmstead's paper on the Ives colorimeter showed the value of this instrument for comparing color values and also as a test for color blindness. Mr. C. F. Woods, in his paper on trolley wires, called attention to the fact that the average weight of a trolley wire is 2000 pounds to the mile; that there are many defects in the manufacture and that great trouble is caused on account of the lack of proper specifications. With a hard-drawn wire, about 0.392 inch diameter, or No. 2 B. & S. gauge would prove the most suitable; that the distance between spans averaged 100 feet. Three conditions, the pull due to its weight, the severe pounding of the trolley wheel and the wave motion

were disturbing features in the life of a trolley line. The qualities required are: homogeneity and flexibility, indicated by the elastic limit, high tensile strength, proper conductivity measured by the Wheatstone bridge, and proper torsional strength. Lake copper has proved the best for general use and next to this electrolytic copper. Practical methods of manufacture were then touched upon and an interesting discussion followed the paper.

Prof. Chas. E. Munroe spoke on the manufacture of amorphous calcium phosphide, calling attention to its use in the Whitehead torpedo.

The following officers of the Division were elected for 1909: *Chairman*, A. D. Little; *Vice-Chairman*, Geo. C. Stone; *Secretary*, B. T. B. Hyde; *Executive Committee, ex officio*, Chairman, Vice Chairman and Secretary, and Editor of the *Journal of Industrial and Engineering Chemistry;* Wm. H. Walker; W. C. Ebaugh; J. O. Handy; A. S. Cushman; and C. P. Van Gundy.

The Chairman of the Division, Dr. A. D. Little, outlined a policy for the Division and suggested that committees be appointed to follow up the various suggestions. There were several definite undertakings which should presently interest the Division of Industrial Chemists and Chemical Engineers. For instance, the matter of trade terms; again, trade customs, both of which would require a careful and comprehensive study which would be appreciated by all present, in view of the many difficulties which arose in general business transactions, due to the lack of definitions in these two important factors. Specifically, the need of defining cylinder oils by trade terms and the decided need of specification for buyer and seller, which should receive the endorsement of the Division were mentioned. The matter of research problems to be taken up in industrial laboratories attached to the universities should arouse the Division's interest and, among other things, work on the spontaneous combustion of coal. A Committee on Publicity would serve many of the needs of the Division and should include a manufacturers' descriptive bibliography.

The following By-Laws were adopted for the government of the Division:

By-laws of the Division of Industrial Chemists and Chemical Engineers.

ARTICLE 1.

MEMBERSHIP.

Membership in the Division shall be open to all members of the American Chemical Society, and any member of the Society shall upon request to the Secretary of the Division be registered as a member of the Division.

ARTICLE 2.

OFFICERS.

1. The officers of the Division shall be a Chairman, a Vice-Chairman, a Recording Secretary and an Executive Committee.

2. The Chairman, Vice-Chairman, Secretary and Editor of the *Journal of Industrial and Engineering Chemistry* shall be members of the Executive Committee *ex officio.*

3. The Chairman of the Division shall be Chairman of the Executive Committee.

4. The Executive Committee shall consist of five registered members of the Division and the members *ex officio* provided by Section 2 of this article.

5. All officers of the Division shall be elected annually by ballot at the last session of the Division held during the annual meeting of the Society and shall take office on January 10th, following the meeting at which they were elected. They shall hold office for one year or until their successors are elected.

6. The Executive Committee shall fill any vacancies occurring through death or resignation among officers of the Division.

7. It shall be the duty of the Chairman to represent the Division in the Council of the Society, to preside at meetings of the Executive Committee, to carry into effect the decisions and recommendations of that committee, to preside at stated meetings of the Division, and to report to the Society at its regular meetings.

8. In the absence of the Chairman, the duties of the office shall devolve upon the Vice-Chairman. The Vice-Chairman shall be *ex officio* Chairman of the Committee on Research Problems.

9. It shall be the duty of the Recording Secretary to keep a record of the proceedings of the Division and of the Executive Committee, to maintain a list of registered members, to send to registered members such notices as the business of the Division may require, and to transmit to the Secretary of the Society the names of all the officers and standing committees of the Division within three weeks of their appointment; and, in like manner, to notify the Secretary of the Society of any change of officers or standing committees during the year.

10. The Recording Secretary shall be the custodian of the files of the Division. He shall have charge of the funds of the Division and shall make all disbursements, subject to the authorization of the Executive Committee. He shall report to the Division at its annual meeting.

11. The Executive Committee shall conduct the business of the Division and direct its activities. The committee shall at each general meeting of the Society and as early as may be, hold a meeting to consider the affairs of the Division and receive reports of its committees. The voting majority of the Executive Committee shall be responsible for all expenditures which it may authorize except so far as the action of the Council shall previously have provided for such expenditure.

ARTICLE 3.

MEETINGS.

There shall be a meeting of the Division at each general meeting of the Society. Business affecting the organization of the Division shall be transacted only at the meeting coincident with the annual meeting of the Society.

The order of business shall be as follows: Reading of Minutes, Report of Executive Committee, Report of Secretary, Report of Committees and Discussions, Reading of Papers and Discussions, Miscellaneous Business, and at the annual meeting, Election of Officers, Unfinished Business.

The regular order of business of the Division may be suspended at any session by the consent of three-fourths of the members of the Society present.

ARTICLE 4.

SPECIAL COMMITTEES.

The Chairman shall with the advice and approval of the Executive Committee appoint from time to time standing

committees of the Division to consider, conduct, and report upon such special matters as may be delegated to them. The following committees shall be appointed at the annual meeting or as soon thereafter as may be expedient.

1. Committee on Definition of Trade Terms; 2. Committee on Trade Customs; 3. Committee on Official Specifications; 4. Committee on Research Problems; 5. Committee on Standard Methods; 6. Committee on Descriptive Bibliographies; 7. Committee on Advertising.

ARTICLE 5.

PUBLICATIONS.

The official organ of the Division shall be the *Journal of Industrial and Engineering Chemistry*.

The Executive Committee may at its discretion provide for the issue of other non-serial publications for distribution to registered members of the Division or for sale.

ARTICLE 6.

ASSESSMENTS.

The Executive Committee may at its discretion impose dues not to exceed three dollars per year upon registered members of the Division, said dues to be collected by the Secretary and the receipts therefrom to be devoted to the purposes of the Division.

ARTICLE 7.

AMENDMENTS

These By-laws may be amended at any annual meeting of the Division by a three-fifths vote of the registered members present, provided two weeks' notice of the proposed amendment with the text thereof has been sent to the registered members of the Division. Amendments to be effective must be approved by the Council and accepted by that body as not inconsistent with the Constitution and By-laws of the Society.

DIVISION OF FERTILIZER CHEMISTS.

The first semi-annual meeting of the Division of Fertilizer Chemists, of the American Chemical Society, was held at Baltimore, December 29th to January 2nd, in connection with the general meeting of the Society. The meeting was called to order by the Chairman, Mr. F. B. Carpenter, and the following program was presented: F. B. Carpenter, The Fertilizer Industry—an historical sketch, (Chairman's address). Arthur Lowenstein, Some Points of Interest in Connection with Present Fertilizer Laws and Proposed Fertilizer Legislation; J. E. Breckenridge, Potash Experiments in Factory Work, showing heavy loss by Official Method; M. H. Pingree, A Comparison of Various Methods in Bringing About the Solution of Potash in Mixed Fertilizers and Tobacco Stems; Geo. D. Leavens, A Discussion of Methods for Determining the Availability of Phosphoric Acid in Thomas Phosphate Powder; F. P. Veitch, A Discussion of Methods for the Determination of Iron and Alumina in Phosphate Rock; F. B. Carpenter, Note on the Determination of Insoluble Phosphoric Acid; Lucius P. Brown, Chemistry and Geology of the Inland Phosphates of the United States; F. B. Porter, Loss of Potash in Commercial Fertilizers; A. G. Stillwell, Remarks on the Gladding Method for Phosphoric Acid (weighing direct the phosphomolybdate precipitate).

The following officers were elected for the year 1909: *Chairman*, F. B. Carpenter; *Vice-Chairman*, B. H. Hite; *Secretary*, J. E. Breckenridge; *Executive Committee*, the Chairman, Vice-Chairman and Secretary *ex-officio*, and Messrs. P. Rudnick and T. S. Gladding. Two committees were appointed, one to draw up By-laws for the government of the division and the other to endeavor to draw up further specifications for the ammonium citrate solution as used in the determination of available phosphoric acid.

The *Journal of Industrial and Engineering Chemistry* hopes that the Division of Fertilizer Chemists will have a long and successful career.

CONVOCATION WEEK MEETING OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Baltimore, December 26, 1908, to January 2, 1909.

The Convocation Week meeting of the American Association for the Advancement of Science broke all previous records for scientific meetings in this country. The registration at the meeting was approximately 1200, and considering the fact that large numbers of scientists in attendance did not register, it is estimated that the attendance may have been as great as 2500. Of the 400 chemists in attendance only about 80 registered and it is likely that the ratio was nearly as small in some of the other affiliated societies. The meeting was so large, and the number of papers (about 1000) so great, that the question of organizing the next meeting is being now seriously considered. Several plans have been proposed and doubtless will be considered by those in authority before the next Convocation Week meeting.

The meetings of Section C and the American Chemical Society are reported elsewhere in this issue, and space will not permit a description of the events and meetings held by the Association. For this our readers are referred to the current numbers of *Science*.

The next Convocation Week Meeting will be held at Boston, December 27, 1909, to January 1, 1910, and after that, the following places in succession have been suggested for Convocation Week meetings: Minneapolis, Washington, Cleveland and Toronto.

In the summer of 1910 it is proposed that the Association meet in Honolulu.

The officers for the coming year are as follows: *President*, David Starr Jordan, Leland Stanford, Jr., University, California; *Vice-Presidents*, Mathematics and Astronomy, E. W. Brown, Yale University, New Haven, Conn; Physics, L. A. Bauer, Carnegie Institute, Washington, D. C.; Chemistry, Wm. C. McPherson, Ohio State University, Columbus, Ohio; Mechanical Science and Engineering, John F. Hayford, U. S. Coast & Geodetic Survey, Washington, D. C.; Geology and Geography, R. W. Brock, School of Mining, Kingston, Ontario; Zoology, W. E. Ritter, University of California, Berkeley, Cal.; Botany, D. P. Penhallow, McGill University, Montreal, Canada; Anthropology and Psychology, W. H. Holmes, Bureau of American Ethnology, Washington, D. C.; Social and Economic Science, Carroll D. Wright, Clark College, Worcester, Mass.; Physiology and Experimental Medicine, C. S. Minot, Harvard Medical School, Boston, Mass.; Education, James E. Russell, Columbia

University, New York City. *Permanent Secretary*, L. O. Howard, Smithsonian Institution, Washington, D. C. *General Secretary*, Dr. D. C. Miller, Case School of Applied Science, Cleveland, Ohio. *Secretary of the Council*, F. S. Benedict, Carnegie Institute, Washington, D. C. *Secretaries of the Sections:* A—Mathematics and Astronomy—Geo. A. Miller, University of Illinois; B—Physics—A. D. Cole, Ohio State University, Columbus, Ohio; C—Chemistry—C. H. Herty, University of North Carolina, Chapel Hill, N. C.; D—Mechanical Science and Engineering—G. W. Bissell, Michigan Agricultural College, East Lansing, Mich.; E—Geology and Geography—F. P. Gulliver, Norwich, Conn.; F—Zoology—Maurice A. Bigelow, Columbia University, New York City; G—Botany—H. C. Cowles, University of Chicago; H—Anthropology and Psychology—George Grant McCurdy, Yale University, New Haven, Conn.; I—Social and Economic Science—J. Pease Norton, Yale University, New Haven, Conn.; K—Physiology and Experimental Medicine—George T. Kemp, University of Illinois, Urbana, Ill.; L—Education—C. R. Mann, University of Chicago, Chicago, Ill. *Treasurer*, R. S. Woodward, Carnegie Institute, Washington, D. C.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

Pittsburg Meeting, December 28 and 29, 1908.

The first annual meeting of the American Institute of Chemical Engineers was held at the Carnegie Technical Schools, Pittsburg, December 28 and 29, 1908. The following papers were read: Wm. M. Booth, Steam Power Plant Economics from the Standpoint of the Chemical Engineer; Edward Gudeman, Technical Coal Analysis; J. C. Wm. Greth, The Chemical Aspect of Impurities which Cause Scale and Corrosion of Steam Boilers; A. Bement, Testing and Performance of Steam Generating Apparatus; H. August Hunicke, The Examination of Flue Gases in Boiler Tests; Ernest Schmatolla, Producer Gas Installations; Richard K. Meade, Heating of Industrial Furnaces with Pulverized Fuel; Edwin T. Northrup, Modern Electrical Resistance Pyrometry; J. A. De Cew, Chemical Specifications for Sulphite Pulp; F. W. Frerichs, An Apparatus for Testing Liquefied Ammonia Gas; J. Herbert Brewster, The Sanitary Condition of the Southern End of Lake Michigan; Thorn Smith, Some Experiments with the Ferric Iron Contact Method of Making Sulphuric Acid from Smelter Fumes; Wm. M. Grosvenor, Drier Calculations and Drier Design.

The papers read and presented were referred to a Publication Committee for publication in a volume of Proceedings or Transactions of the Institute. The following officers were elected: *President*, Samuel P. Sadtler, Philadelphia, Pa.; *Vice-Presidents*, Chas. F. McKenna, New York City; H. A. Hunicke, St. Louis, Mo.; Edw. G. Acheson, Niagara Falls, N. Y.; *Secretary*, John C. Olsen, Brooklyn, N. Y.; *Treasurer*, Wm. M. Booth, Syracuse, N. Y.; *Auditor*, Richard K. Meade, Nazareth, Pa.; *Directors*, Ludwig Reuter, Berkeley, Calif.; Thorn Smith, Isabella, Tenn.; H. F. Brown, Wilmington, Del.; Eugene Haanel, Ottawa, Can.; J. M. Camp, Duquesne, Pa.; Charles A. Catlin, Providence, R. I.; George P. Adamson, Easton, Pa.; David Wesson, Montclair, N. J.; Edward Gudeman, Chicago, Ill.

The next meeting will be held in June, 1909, the exact time and place to be announced later.

UTAH SOCIETY OF ENGINEERS.

The November meeting of the Utah Society of Engineers was held in the Chemistry Lecture Room of the University of Utah on the 21st of the month. Papers were presented as follows:

"Suction Gas Producer Plants" (illustrated), by F. E. Johnson, of the Fairbanks-Morse Co.

"Short and Easy Methods for Calculating the Carrying Capacity of Pipes and Open Channels," by Richard R. Lyman, Univ. of Utah.

At the December meeting of the Society, held at the Commercial Club on the 19th, the papers were as follows:

"Smelter Smoke Treatment," by W. C. Ebaugh, Univ. of Utah.

"Lead Losses in the Blast Furnace," by Richard D. McCaffrey, consulting engineer.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

London May 27 to June 2, 1909.

The Seventh International Congress of Applied Chemistry will meet in London from May 27 to June 2, 1909. The Congress is under the patronage of His Majesty The King, and vice-patronage of His Royal Highness The Prince, of Wales. The President of Honor is Sir Henry Roscoe and the active President Sir William Ramsay, Mr. Wm. Macnab is general secretary and Messrs. Thos. Tyrer and C. Wightman are treasurers.

The Congress is divided into the following sections and sub-sections:

1. Analytical Chemistry, Dr. T. E. Thorpe, C.B., F.R.S.
2. Inorganic Chemistry and Allied Industries, Dr. Ludwig Mond, F.R.S.
3. Metallurgy and Mining Explosives:
   (a) Metallurgy and Mining, Sir Hugh Bell, Bart.
   (b) Explosives, Sir Andrew Noble, Bart., K.C.B., F.R.S.
4. Organic Chemistry and Allied Industries:
   (a) Organic Products, Prof. W. H. Perkin, F.R.S.
   (b) Coloring Substances and Their Uses, Prof. Meldola, F.R.S.
5. Industry and Chemistry of Sugar, Richard Garton, Esq.
6. Starch Industry:
   (a) Starch Industry, Dr. Horace T. Brown, F.R.S.
   (b) Fermentation, John Gretton, Esq., M.P.
7. Agricultural Chemistry, Lord Blyth.
8. Hygiene, Medical and Pharmaceutical Chemistry—Bromatology:
   (a) Hygiene and Medical Chemistry, Sir J. Crichton Brone, F.R.S.
   (b) Pharmaceutical Chemistry, N. H. Martin, Esq.
   (c) Bromatology, Robert R. Tatlock, Esq., F.I.C.
9. Photographic Chemistry, Sir W. de W. Abney, K.C.B., F.R.S.

10. Electrical and Physical Chemistry, Sir John Brunner, M.P.
11. Law, Political Economics and Legislation with reference to Chemical Industries, Lord Alverstone.

The American Committee is organized as follows:

Dr. Harvey W. Wiley, Chairman American Committee, Washington, D. C.

Members of the Advisory Committee of Honor.

Dr. John J. Abel, President of the American Society of Biological Chemists, Johns Hopkins University, Baltimore, Maryland, U. S. A.; Mr. Edward G. Acheson, President of the American Electrochemical Society, International Acheson Graphite Company, Niagara Falls, New York, U. S. A.; Dr. M. T. Bogert, President of the American Chemical Society, Columbia University, New York City, U. S. A.; Dr. C. F. Chandler, former President of the American Chemical Society, head of the Chemical Department of Columbia University, Columbia University, New York City, U. S. A.; Dr. Frank W. Clarke, former President of the American Chemical Society, and honorary member of the English Chemical Society, Geological Survey, Washington, D. C., U. S. A.; Dr. Wm. H. Nichols, Chairman of the General Chemical Company, 25 Broad Street, New York City, U. S. A.; Dr. Ira Remsen, President of the Johns Hopkins University, former President of the American Chemical Society, Johns Hopkins University, Baltimore, Maryland, U. S. A.

SECTION 1. ANALYTICAL CHEMISTRY.

Chas. Baskerville, Chairman, The College of the City of New York, New York City, U. S. A.; T. L. Briggs, 25 Broad Street, New York City, U. S. A.; Louis Munroe Dennis, Cornell University, Ithaca, New York, U. S. A.; Parker, C. McIlhiney, 7 East 42nd Street, New York City, U. S. A.; Henry P. Talbot, Massachusetts Institute of Technology, Boston, Massachusetts, U. S. A.; Fletcher P. Veitch, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., U. S. A.; Percy H. Walker, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., U. S. A.

SECTION 2. INORGANIC CHEMISTRY.

J. D. Pennock, Chairman, The Solvay Process Company, Syracuse, New York, U. S. A.; A. S. Cushman, Office of Public Roads, U. S. Department of Agriculture, Washington, D. C., U. S. A.; Clifford Richardson, Cortlandt Street Building, 32 Church Street, New York City, U. S. A.; Wm. D. Richardson, care Swift & Co., Chicago, Illinois, U. S. A.; W. H. Walker, Massachusetts Institute of Technology, Boston, Massachusetts, U. S. A.

SECTION 3. METALLURGY AND MINING. EXPLOSIVES.

Division a. Metallurgy and Mining.

John Hays Hammond, Chairman, 71 Broadway, New York City, U. S. A.; F. P. Dewey, 415–6 Colorado Building, Washington, D. C., U. S. A.; H. O. Hofman, Massachusetts Institute of Technology, Boston, Massachusetts, U. S. A.; N. W. Lord, Ohio State University, Columbus, Ohio, U. S. A.; J. W. Richards, Bethlehem, Pennsylvania, U. S. A.; R. H. Richards, Massachusetts Institute of Technology, Boston, Massachusetts, U. S. A.; Albert Sauveur, Cambridge, Massachusetts, U. S. A.; Thomas D. West, Sharpsville, Pennsylvania, U. S. A.

Division b. Explosives.

Chas. E. Munroe, Chairman, The George Washington University, Washington, D. C., U. S. A.; A. A. Breneman, 97 Water Street, New York City, U. S. A.; Arthur M. Comey, E. I. duPont de Nemours Powder Co., Chester, Pennsylvania, U. S. A.; Clarence Hall, U. S. Testing Station, 40th and Butler Streets, Pittsburg, Pennsylvania, U. S. A.; G. W. Patterson, U. S. Smokeless Powder Factory, Indian Head, Maryland, U. S. A.

SECTION 4. ORGANIC CHEMISTRY AND ALLIED INDUSTRIES.

Division a. Organic Chemistry.

William McMurtrie, Chairman, 480 Park Avenue, New York City, U. S. A.; F. D. Dodge, 69 Avenue A., Bayonne, New Jersey, U. S. A.; A. H. Gill, Massachusetts Institute of Technology, Boston, Massachusetts, U. S. A.; W. S. Gray, 76 William Street, New York City, U. S. A.; Arthur Lachman, Petaluma, California, U. S. A.; A. H. Sabin, 432 Sanford Avenue, Flushing, New York, U. S. A.; Homer E. Sawyer, 42 Broadway, New York City, U. S. A.

Division b. Coloring Substances and Their Uses.

Bernhard C. Hesse, Chairman, 90 William Street, New York City, U. S. A.; Herman A. Metz, Comptroller of the City of New York, New York City, U. S. A.; Hugo Schweitzer, 427 West 117th Street, New York City, U. S. A.; I. F. Stone, 100 William Street, New York City, U. S. A.; Louis I. Waldman, Box 162, Albany, New York, U. S. A.

SECTION 5. INDUSTRY AND CHEMISTRY OF SUGAR.

Charles A. Browne, Chairman, Mallery Building, 80 South Street, New York City, U. S. A.; A. Hugh Bryan, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., U. S. A.; David L. Davoll, care Guantanomo Sugar Co., Guantanomo, Cuba; Hubert Edson, Guanica Centrale, Porto Rico; Wm. D. Horne, Yonkers, New York, U. S. A.

SECTION 6. STARCH INDUSTRY.

Division a. Starch Industry.

T. B. Wagner, Chairman, Heyworth Building, Chicago, Illinois, U. S. A.; Arno Behr, Pasadena, California, U. S. A.; Henry Carmichael, Columbia University, New York City, U. S. A.; George J. Jenks, Huron Milling Company, Harbor Beach, Michigan, U. S. A.; George W. Rolfe, Institute of Technology, Boston, Massachusetts, U. S. A.

Division b. Fermentation.

Francis Wyatt, Chairman, 402 West 23rd Street, New York City, U. S. A.; Carl Glaser, 22 South Gay Street, Baltimore, Maryland, U. S. A.; Julius Liebmann, 109–111 East 15th Street, New York City, U. S. A.; Samuel C. Prescott, 739 Boylston Street, Boston, Massachusetts, U. S. A.; A. J. Schedler, Pabst Brewing Co., Milwaukee, Wisconsin, U. S. A.

SECTION 7. AGRICULTURAL CHEMISTRY.

C. G. Hopkins, Chairman, University of Illinois, Urbana, Illinois, U. S. A.; R. J. Davidson, Virginia Polytechnic Institute, Blacksburg, Virginia, U. S. A.; J. G. Lipman, New Jersey Agricultural College, Experiment Station, New Brunswick, New Jersey, U. S. A.; F. T. Shutt, Dominion Agricultural College Manhattan, Kansas, U. S. A.; Experimental Farms, Ottawa, Canada; J. T. Willard, Kansas.

SECTION 8. HYGIENE, MEDICAL AND PHARMACEUTICAL CHEMISTRY. BROMATOLOGY.

Division a. Hygiene and Medical Chemistry.

Reid Hunt, Chairman, Hygienic Laboratory, U. S. Public Health and Marine Hospital Service, Washington, D. C., U. S. A.; William J. Gies, 437 West 59th Street, New York City, U. S. A.; Walter S. Haines, Rush Medical College, University of Chicago, Chicago, Illinois, U. S. A.; M. E. Jaffa, University of California, Berkeley, California, U. S. A.; Walter Jones, Johns Hopkins University, Baltimore, Maryland, U. S. A.; John Marshall, University of Pennsylvania, Philadelphia, Pennsylvania, U. S. A.

Division b. Pharmaceutical Chemistry.

Joseph P. Remington, Chairman, 1832 Pine Street, Philadelphia, Pa., U. S. A.; Virgil Coblentz, Columbia University, New York City, U. S. A.; Edward Kremers, University of Wisconsin, Madison, Wisconsin, U. S. A.; A. B. Lyons, 72 Brainard Street, Detroit, Michigan, U. S. A.; Samuel P. Sadtler, N. E. Corner Tenth and Chestnut Streets, Philadelphia, Pennsylvania, U. S. A.

Division c. Bromatology.

W. D. Bigelow, Chairman, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., U. S. A.; E. M. Chamot, Cornell University, Ithaca, New York, U. S. A.; Chas. F. Langworthy, Office of Experiment Stations, U. S. Department of Agriculture, Washington, D. C., U. S. A.; Graham Lusk, 11 East 74th Street, New York City, U. S. A.; W. W. Skinner, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., U. S. A.

SECTION 9. PHOTOGRAPHIC CHEMISTRY.

L. H. Baekeland, Chairman, Yonkers, New York, U. S. A.; L. H. Friedburg, The College of the City of New York, New York City, U. S. A.; Frank W. Lovejoy, Eastman Kodak Company, Rochester, New York, U. S. A.; Henry M. Reichenbach, Yonkers, New York, U. S. A.; Maximilian Toch, 320 Fifth Avenue, New York City, U. S. A.

SECTION 10. ELECTRICAL AND PHYSICAL CHEMISTRY.

W. D. Bancroft, Chairman, 7 East Avenue, Ithaca, New York, U. S. A.; Chas. A. Doremus, 55 West 53rd Street, New York City, U. S. A.; F. A. J. FitzGerald, FitzGerald and Bennie Laboratories, Niagara Falls, New York, U. S. A.; L. Kahlenberg, University of Wisconsin, Madison, Wisconsin, U. S. A.; E. R. Taylor, Penn Yan, New York, U. S. A.; W. R. Whitney, General Electric Company, Schenectady, New York, U. S. A.

SECTION 11. LAW, POLITICAL ECONOMICS AND LEGISLATION WITH REFERENCE TO CHEMICAL INDUSTRIES.

Chas. B. Dudley, Chairman, Altoona, Pennsylvania, U. S. A.; David T. Day, Geological Survey, Washington, D. C., U. S. A.; Russell W. Moore, U. S. Customs Service, New York City, N. Y.; Wm. J. Schieffelin, 81 Fulton Street, New York City, U. S. A.; S. P. Sharples, 26 Broad Street, Boston, Massachusetts, U. S. A.; Geo. C. Stone, 71 Broadway, New York City; David Wesson, 24 Broad Street, New York City, U. S. A.

The price of membership is one pound for men and fifteen shillings for women. American chemists intending to become members should send check for five dollars ($5.00) either to one of the Chairmen of the Sections or directly to the Chairman of the American Committee at Washington.

Those intending to present papers should write to the Chairman of the Section to which the paper belongs. All papers should be neatly typewritten on thin paper and should be in the hands of the Chairman of the American Committee not later than April 1, 1909, in order to be forwarded to London to be translated and printed for use of the members of the Congress. It is earnestly hoped that a very large membership will be secured. Those who can not attend will be amply rewarded for the membership by receiving the publications which will be in several large volumes and which will contain the latest ideas and discoveries connected with the idea of applied chemistry.

H. W. WILEY.

At the meeting of the 25th annual convention of the Association of Official Agricultural Chemists held in Washington, D. C., November 12th to 16th inclusive, the following recommendations by the referees in charge of the work on "Soils and Fertilizers" were adopted:

POTASH.

(1) That the cobalti-nitrite method for potash be tested during the coming year.

(2) That there be a further trial of the method involving the use of ammonium hydroxide and ammonium oxalate in the preparation of the solution in the determination of the potash in potash salts, as compared with the present method of direct precipitation of the potash without the use of the reagents mentioned.

The referee stated that he had not been able to take up the extensive investigations that would be necessary in attempting to define available potash, and offered the following resolution which was passed by the association:

Resolved, That in view of the fact that practically the entire available time of the referee on potash is needed for the study of analytical methods, the investigation of the question of determining what should be designated as "available potash" provided for in a resolution adopted in 1906, be undertaken by a special referee or associate referee.

PHOSPHORIC ACID.

(1) That the recommendation of 1907 be repeated, namely, that the referee on phosphoric acid shall take up for report, at the next meeting of the association, methods applicable under American conditions to the official examination of basic slag phosphates.

(2) That the referee make a further study of methods for the preparation of neutral ammonium citrate.

(3) That the referee investigate the amount of wash water to be employed in the treatment of the residue from the ammonium citrate digestion.

This recommendation was amended to include a study of the manner of filtering, and was so adopted.

SOILS.

(1) That the modified J. L. Smith method for total potassium be adopted as a provisional method and be further studied (Cir. **32**, p. 4).

This recommendation was adopted in the modified form, as presented by the committee, the referee having recommended its adoption as an optional method.

(2) That the sodium peroxide fusion for total phosphorus be continued as a provisional method and be further tested (Bull. **105**, p. 145).

This recommendation also was adopted in the form presented by the committee, the referee having recommended the adoption of the method as official.

(3) That the magnesium nitrate method for total phosphorus be adopted as a provisional method and be further tested.

(4) That the Knorr method for the determination of carbonates in soils be further studied (Wiley's "Principles and Practice of Agricultural Analysis," Vol. 1, ed. 1894, p. 338; ed. 1906, p. 380).

The magnesium nitrate method as outlined by the referee reads as follows:

Magnesium nitrate method for total phosphorus in soils—provisional.

Weigh into a 50 cc. porcelain dish 5 grams of salt.

Moisten with 5 to 7 cc. of magnesium nitrate solution (Bull. **107,** Rev., page 2, sec. (g)), bring to dryness on the water bath, burn off the organic matter at low redness, when cool moisten slightly with water, add 10 cc. of concentrated hydrochloric acid, and digest 2 hours on the water bath, keeping the dish covered with a watch glass and stirring two or three times during digestion.

Make up to 250 cc., mix well, and throw on a dry folded filter, pouring back on the filter until the solution runs through clear.

Make the determination on aliquots corresponding to 2 or 4 grams of the soil, depending upon the amount of phosphorus present. Bring to dryness, take up with hydrochloric acid and water, and filter over a pump. Filtrate and washings should not exceed 30 to 40 cc. Make alkaline with ammonium hydroxide, and dissolve the precipitate with concentrated nitric acid, using a slight excess. Add gradually, while shaking, 5 to 15 cc. of molybdate solution (Bull. **107,** Rev., page 2). Let stand a minute or two and add 15 cc. of ammonium nitrate (Bull. **107,** Rev., page 2), shaking thoroughly. Keep the solution at 40° to 50° C. for an hour, let stand over night at room temperature, filter[1] and wash well with cold water. Put filter and precipitate back into the same flask, using as little wash water as possible. Determine phosphorus volumetrically, using standard potassium hydroxide and nitric acid.

[1] A Hirsch funnel, with a double qualitative filter S. and S. No 597, cut to fit and pressed down well around the edge after wetting and putting on pressure, is recommended.

The eighth annual meeting of the Board of Trustees of the Committee of Revision of U. S. Pharmacopoeia, was held at Boston, May 23 to 25, 1908. Arrangements were made for placing the Spanish edition of the Pharmacopoeia on the market. It was also decided to publish a Digest of Comments on the eighth revision; these are to serve as aid in the next revision of 1910.

The 56th annual meeting of the American Pharmaceutical Association convened at Hot Springs, Arkansas, Sept. 7th to 12th. The able address of the President, Prof. Searby, of San Francisco, was devoted to Pharmaceutical educational subjects. Before the Scientific Section (Chairman, V. Coblentz), the more important papers presented were: The Crystalline Alkaloid of Calycanthus Glaucus—H. M. Gordin; Differences in the Structure of Belladonna and Scopola—H. Kraemer; The Estimation of Phenol—W. A. Puckner and A. H. Clark; Proteid Compounds of Heavy Metals—H. A. Dunning; Notes on the Estimation of Hydrastine—F. R. Eldred and C. M. Pence; Detection of Phenol and Cresotic Acids in Salicylic Acid—H. Engelhard and H. W. Jones; Deterioration of Hydrocyanic Acid, Volumetric Estimation of Phosphoric Acid, Quantity of Arsenic Present in Bismuth Salts—V. Coblentz and O. May; Standardization of Digitalis Preparations—C. E. Vanderkleed and E. Reed; The Superiority of Artificial Mineral Waters—E. Sander; Further Study of the Alkaloids of Gelsemium—L. E. Sayre, etc.; Officers elected for the ensuing year are: *Prest.*, Prof. O. Oldberg (Chicago); *Treas.*, Dr. H. M. Whelpley (St. Louis); *Gen. Sec'y*, Prof. Chas. Caspari, Jr. (Baltimore).

The time and place of the next meeting will be announced later. Total membership of the Association is 2,151.

COMMITTEE 24, INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS.

This committee, of which Prof. Henry M. Howe is chairman, deals with the question of Uniform Nomenclature of Iron and Steel. They have published a report in four parts:

(1) A polyglot of the names of the different varieties of iron and steel in English, French, German, Swedish, Danish and Dutch, together with the names of the apparatus in which they are usually made.

(2) Definitions of the principal classes of iron and steel in English.

(3) A glossary of special size and shapes of iron and steel.

(4) A note on the boundary between steel and cast-iron.

WM. CAMPBELL.

COMMITTEE ON THE ANALYSIS OF FATS, SOAPS AND GLYCERINE.

A meeting of the Committee on the Analysis of Fats, Soaps and Glycerine was held at the Hotel Belvedere, on Tuesday evening, December 29th. After listening to the reports of the special committees on the analysis of various products, it was decided that samples of the various products should be sent out not later than February first, to the largest list of chemists who had agreed to co-operate in the analytical work. Where the work entailed a large number of determinations, it was decided to take up the different determinations in small groups, two or three at a time, until the entire subject was covered.

It was decided to hold the next meeting of the Committee at Detroit, at the time of the summer meeting of the American Chemical Society.

At the meeting of the Verein Deutscher Chemiker (Pharm. Chem. Section) held on Nov. 20, 1908, the papers read were: "The Estimation of Iodine in Iodoform and Thymol Iodide," and "The Estimation of Metallic Iron in Ferrum Reductum."

MILWAUKEE SECTION, AMERICAN CHEMICAL SOCIETY.

The recently organized Milwaukee Section of the American Chemical Society held its first banquet and meeting at

the Plankington House, Milwaukee, January 14, 1909. The meeting was attended by 125 members and guests including a number of prominent manufacturers and superintendents. Two papers were read: the first by Mr. W. D. Richardson, of Chicago, entitled "Bernard Palissy, a Chapter from the Industrial Foundation of Chemistry;" the second by Prof. C. F. Burgess, of the University of Wisconsin, on the "Corrosion of Iron and Steel," illustrated with lantern slides. A lively and interesting discussion followed. The officers of the Section are: *Chairman*, Martin M. Rock; *Vice-chairman*, A. W. Gregg; *Secretary*, J. H. Linton; *Treasurer*, E. V. Manuel.

PERSONAL NOTES.

Mr. William J. Schieffelin was elected, on December 28th, chairman of the Citizens Union, of New York, to succeed R. Fulton Cutting. Mr. Schieffelin is president of Schieffelin & Company, of New York, and has been associated with many public movements.

F. E. Dodge, secretary of the Philadelphia Section of the American Chemical Society, has recently accepted a position as general manager of the Art Fibre Company, of Norristown, Pa.

D. W. Horn is consulting chemist to the Art Fibre Company, of Norristown, Pa.

Dr. Edward Gudeman, of Chicago, sailed on December 31st for Havana, Cuba, to look after his interests at that place.

Dr. G. W. Gray, formerly chief chemist with the Standard Oil Company, at Whiting, Ind., and recently with independent interests in Kansas, has gone to Bay View, New Jersey, to take charge of the laboratory in the new Standard Oil plant at that place.

The official announcement of the award of the Nobel prizes for the year 1908 is as follows:

Literature.—Prof. Rudolf Eucken, of Jena University, who has written much on philosophical subjects.

Physics.—Prof. Gabriel Lippman, of the University of Paris.

Chemistry.—Prof. Ernest Rutherford, director of the physical laboratory of the University of Manchester, England.

Medicine.—Divided between Dr. Paul Ehrlich, of Berlin, and Prof. Elie Metchnikoff, of the Pasteur Institute, Paris.

INDUSTRIAL AND TRADE NOTES.

The Chicago Second Annual Cement Show will be held in the Coliseum Building, February 18th to 24th. President Edw. W. Hagar expects 250 exhibitors, representing a capital of $250,000,000 to be represented. Thomas A. Edison will deliver the opening address and will also exhibit the castings by which a complete residence can be poured and cast in one day.

Following the great earthquake in Sicily, the price of lemon oil has gone from $0.80 per lb. to $3.00 per lb. and oil of bergamot from $3.00 to about $12.00 per lb.

A merger of independent fertilizer interests financed by J. P. Morgan & Co., has been incorporated under the name of the Independent Fertilizer Company. The capital will be $50,000,000, equally divided between common and preferred stock. For the present, the corporation will issue only $30,000,000 of this amount, divided in $15,000,000 common and $15,000,000 preferred. The output of the company, it is stated, will be 1,000,000 tons as contrasted with 2,000,000 when the merger was first considered. Forty companies distributed from Maryland to Florida and several in the west are interested, as well as potash interests of Waldemar Schmidtman in Germany. The main office of the company will be in New York.

Phelps, Dodge & Company, incorporated, capitalized at $50,000,000 have taken over the various copper properties of Phelps Dodge & Co., the output of which has been as high as 100,000,000 lbs. a year, including the Copper Queen Consolidated Mining Co., the Montezuma Copper Co., the Detroit Mining Co., of Arizona, and the Stag Canon Fuel Co.

It is reported that the Knapp Mining Co. will continue exploration and development in the newly discovered gold fields in Dunn County, Wisconsin, during the winter. The ore is in the form of decomposed quartz and silver; copper and platinum accompany the gold. In one vein the ore carried an average mining value of $10.00 per ton. A 150-ton cyanide-amalgamation plant will be installed.

At Minas Nuevas in the Parral district of Mexico, the Hidalgo Mining Co. will instal an extensive cyanide plant and make exhaustive tests with different classes of ore.

It is reported that a flowing well of petroleum has been struck between Goldfield, Nevada and Blair, Nevada. The oil shows a paraffine base and will be of great value in the mining region of Nevada.

On December 15th the Fink smelter, constructed at the expense of Samuel Newhouse, the Salt Lake mining operator, was blown in. Salt Lake mining interests are greatly interested in the results of the plant.

Agents of the Japanese government early in December bought from the owner the Pilgrim River (Alaska) antimony mine, the largest in America. The price reported is $100,000.

Cyanide mills are projected for the Nevada Wonder mine at Wonder, Nevada, and for the Bullfrog Diamond mine at Ladd Mountain.

The copper production for Arizona during 1908 approximated 300,000,000 lbs. The Copper Queen mine led with about 8,220,000 lbs., the Calumet and Arizona, and Superior

and Pittsburg yielding 4,940,000 lbs.; the Old Dominion, 3,685,000 lbs.; the Arizona Copper, 3,000,000 lbs.; the Shannon, 1,636,000 lbs.; the Detroit, 2,000,000 lbs.; United Verde, 3,139,000 lbs.: and Imperial, 750,000 lbs.

The coke oven interests of the American Coal Products Co. were turned over, January 1st, to the German American Gas Co., operators for German interests. The capital of the new company will be $2,000,000.

An important find of tin, thirty miles northeast of Eli, Nevada, near the Utah line, was reported early in December. The ore also carries a little tungsten and 11 per cent. to 30 per cent. of tin.

On December 21st, the first blast furnace of the new Indiana Steel Company's plant at Gary, Indiana, was blown in. The furnace is the first of sixteen planned for the plant. The general superintendent of the plant, Mr. W. B. Gleason, delivered an address to the department heads and guests.

The concrete poles along the lines of the Pennsylvania railroad west of Pittsburg are reported to be a success. The poles are 30 feet long, 14 inches in diameter at the bottom and 6 inches at the top.

The hurricane which struck Turk's Island on September 10th, besides doing other damage, flooded great quantities of salt which was stored in the open. The salt ponds were flooded and the total production for the year 1908 is probably not more than half that raked during 1907.

The U. S. Smelting, Refining and Mining Co. has successfully solved the problem of smelter fumes at its lead smelter in Salt Lake valley and has asked the courts for authority to operate its copper smelter again under the court's direction. The company's copper smelter, together with several others, was shut down over a year ago, on account of damage to agricultural interests by smelter fumes.

The representatives of the Anaconda Copper Co. met President Roosevelt at the White House, December 5th, to present their side of the controversy over the destruction of vegetation at Anaconda, against which the farmers of the region had protested. President Roosevelt agreed to make an investigation to ascertain whether a practical method is possible for the extraction of the poisonous substances from the fumes, and will send a representative to Ducktown, Tenn., to investigate sulphur and arsenic recovery plants at that plant. At Butte and Anaconda mass meetings were held to protest against the threatened federal injunction against copper smelter operators.

The now famous Standard Oil case, in which previously a fine of $29,000,000 was imposed, has been remanded for a new trial by the Supreme Court, a writ of *certiorari* petitioned for by the government having been refused.

The Supreme Court of Missouri, on December 23rd, handed down a decision ousting the Standard Oil Company of Indiana and the Republic Oil Company, from the state of Missouri, forbidding them ever again to do business in Missouri and dissolving the Waters-Pierce Oil Company of St. Louis. In addition, each company was fined $50,000.

In the suit to dissolve the Standard Oil Company, of New Jersey, before Ex-Judge Franklin Ferris, John D. Archbold of the company was on the witness stand November 25th and from November 30th to December 5th.

On December 16th the charge was made that peonage existed in connection with the construction of the $10,000,000 plant of the Corn Products Company, at Argo, Ill., fifteen miles from Chicago. The charges were investigated by the Federal Grand Jury. The representatives of the company have denied all the charges.

At the hearings before Chairman Sereno E. Payne's Ways and Means Committee of the House on the tariff, probably the most interesting figures who appeared during December were Andrew Carnegie, E. H. Gary and Chas. M. Schwab. Mr. Carnegie was of the opinion that a duty was no longer necessary on steel produced in the United States. Messrs. Schwab and Gary were quite as firmly in favor of the present tariff. In this connection a most interesting article entitled "My Experiences with, and Views upon the Tariff" by Andrew Carnegie, appeared in the December *Century Magazine*.

A new smelter organization, with New Jersey incorporation, Standard Oil backing and headed by the Cole-Ryan interests, is reported. The smelter now in course of construction for the Utah Consolidated Mining Co. will be the nucleus for several others which will be built on a smaller scale. It is understood that the American Smelting & Refining Co. refused to renew a contract with the Utah Consolidated at the old rate.

Construction work is well under way on the cyanamid plant of the American Cyanamid Company on the Canadian side at Niagara Falls. The plant is being built of concrete, and it is reported will use, when completed, between 60,000 and 70,000 kw. which is contracted for at a low rate with the Ontario Power Co. Three-phase calcium carbide furnaces of the Steffan type will be used, the furnaces being designed abroad. The plant will operate the Caro-Frank cyanamid process under a license from the Societa Italiana per la fabricazione di Produtti Azotati, of Rome, covering the sole right to manufacture and use, distribute and sell calcium cyanamid in the United States, her territories and colonies. Other plants will be established at a later date. The works either in operation or projected in Europe under license from the Societa are as follows: Northwestern Cyanamid Co., of London (ultimate capacity 55,000 tons) Odde, Norway, 13,750 tons; Ostdeutsche Kalkstickstoff Works of Berlin, Mulhthal, Prussia, 3,300 tons; Société Suiss Probera Azotati, Martigny, Switzerland, 4,400 tons; Société Français Pour Produis Azotati of Paris, Notre Dame de Briancon, Savoy, France, 13,200 tons; Cyanamid Gesellschaft of Berlin, Trosberg, Bavaria, 16,500 tons; Societa Italiana pel Carbura di Calcio of Rome, Collestatti, Italy, 13,750 tons; Societa

Italiana pel Carbura di Calcio of Rome (projected), Sebenico Dalmatia, Austria, 27,500 tons; Societa Italiana pel Carburo di Calcio, of Rome (projected), Almissa, Dalmatia, 50,000 tons; San Marcel Company, Italy, 8,250 tons; Societa Italiana per la fabricazione di Produtti Azotati of Rome, Piana d'Orta, Italy, 11,550 tons; Societa Italiana per la fabricazione di Produtti Azotati, of Rome, Fiume, Dalmatia, 4,400 tons.

The use of sulfite pitch (selpech) for briquetting coal in Rhenish Westphalia is reported by Consul George Eager, of Barmen, in *Daily Counsular Report* No. 3361.

A damage suit brought by Shoup and Jaynes *vs.* the Utah Consolidated Mining Co. and the United States Smelting, Refining & Mining Co., for alleged injury to sheep, was decided in favor of the defendants in the United States District Court at Salt Lake City on December 15, 1908. This is one of the few smelter smoke cases that have not resulted in an award of damages.

The United States Smelter at Bingham Junction, Utah, is adding an extension to its bag house to take 1200 bags. The results of bag house treatment of smoke at the two smelters in the Salt Lake valley are quite satisfactory.

The plant of the Inland Crystal Salt Co., at which the salt obtained from the water of Great Salt Lake by solar evaporation was purified, was totally destroyed by fire on the evening of November 5th. The loss is placed at $125,000.00 with $50,000.00 insurance. Plans for rebuilding on an enlarged scale are now under consideration.

The Utah Consolidated Mining Company has made a contract with W. D. Thornton and others, of Butte, for the treatment of its ores at a new smelter to be erected in Tooele Valley, southwest of the Garfield plant of the American Smelting & Refining Co. The statement given to the press by President Broughton, of the Utah Consolidated Company, is as follows:

"This company has now entered into a contract with W. D. Thornton, of Butte, for the smelting of its ores for a period of ten years, commencing April, 1910, the proper performance of which contract is guaranteed by four persons acceptable to the board of directors. Under the provisions of this contract Mr. Thornton agrees:

"(1) To erect a smelting plant in Tooele County, Utah, to be in operation by April, 1910, to treat the output of the mine up to 1200 tons per day, at a rate which is 67.20 cents per ton more favorable to our company than the contract now existing with the Garfield Smelting Company.

"(2) To acquire from this company, at cost, all the lands and options it has acquired in Tooele County.

"(3) To give this company an option upon any part of $500,000.00 par value of the capital stock of the company to be formed to operate the new smelter upon as favorable terms as may be extended to any other subscriber to stock.

"The cost to this company of transporting ore to the Tooele smelter will not exceed 15 cents per ton.

"All figures in connection with the existing contract and that entered into with Mr. Thornton have been approved by E. P. Mathewson, of Anaconda, this company's consulting engineer."

It will be remembered that the smelter of the Utah Consolidated Company near Murray, Utah, is now closed as a result of the injunction granted by the United States Court on complaint of an association of farmers.

The Association of American Portland Cement Manufacturers met at the Hotel Knickerbocker, New York, from December 7, to December 12, 1908. The companies represented have a combined output of 90,000,000 barrels or 92 per cent. of the total output in the United States. In this country there are at present 92 operating cement mills with a combined capacity of 98,534,000 bbls. About 125 new mills are being promoted. In his address, John B. Lober, the president, stated that a review of the cement industry for 1908 shows that for the first time it has reached the condition characteristic of other great industries of the United States.

In the 10 years ending with 1907, production has increased from 2,430,000 pounds to 48,785,000 pounds. The decreased percentage of growth during the last two years indicates that the business has reached a period of ordinary industrial development, and that future development must be based upon normal increase of demand.

Denatured Alcohol in France.

Present Extent of Manufacture—Prices and Influences.—Consul-General Frank H. Mason, of Paris, has prepared the following review of present and prospective conditions affecting the denatured alcohol product in France:

The total production of alcohol in France during the five years ending with 1907 has been as follows, the statistics being given in hectoliters of 100 liters, equal to 26.42 gallons:

Year.	Total production. Hectoliters.	Average wholesale price per hectoliter.
1903	2,047,000	$8.29
1904	2,257,000	8.49
1905	2,609,000	8.68
1906	2,710,000	8.10
1907	2,514,810	8.29

The substances from which the output of alcohol in 1907 were distilled, and the proportion derived from each source, were as follows:

Derivatives.	Hectoliters.	Gallons.
Grains	454,142	11,998,430
Molasses	466,608	12,327,783
Beets	1,145,433	30,262,339
Wines	239,877	6,337,550
Apples and pears	69,283	1,830,456
Grape skins and lees	122,608	3,239,303
Other fruits	16,658	440,104
Various substances	201	5,310
Total	2,514,810	66,441,275

Besides the foregoing native supply, France imported in 1907, mainly from Great Britain and Germany, 153,766 hectoliters (4,062,497 gallons) of alcohol and exported 300,532 hectoliters, being an excess of exports over imports amounting to 146,766 hectoliters, or 3,877,557 gallons. Deducting this excess from the total of production and im-

ports, there remained a supply of 2,368,044 hectoliters (62,563,722 gallons) for the various purposes of consumption.

Production and Consumption.—Alcohol for industrial and other purposes is denatured in France, in presence of a government official, by mixing with each hectoliter, or 26.42 gallons, of spirit the following standard denaturing mixture: 15 liters of methyl alcohol, ½ liter of heavy benzine, 1 gram of malachite green. The cost of these ingredients in the above quantities is about 19.86 francs, or $3.83, which adds that amount to the price of 115½ liters of denatured alcohol and imposes what many consumers consider a burdensome tax on methylated spirits. Notwithstanding this the consumption of denatured alcohol in France is steadily increasing, having grown from 146,529 hectoliters (3,871,296 gallons) in 1897 to 593,836 hectoliters (15,689,147 gallons) in 1907.

The various uses to which denatured spirit is applied and the relative proportion consumed in each during the past five years will be shown by the following table, in which the statistics of consumption are given in hectoliters:

Year.	1903.	1904.	1905.	1906.	1907.
Heating and lighting	262,036	289,748	315,079	374,506	401,230
Varnish	11,580	12,433	11,544	13,444	13,386
Cabinet-making	2,502	1,890	1,757	1,702	1,190
Celluloid, etc	20,095	18,771	21,293	14,589	17,133
Hat manufacture	365	234	228	186	297
Dyes and colors	532	391	554	1,071	632
Rennet, liquid	142	111	148	139	178
Collodion	146	272	417	697	750
Chloroform	377	174	186	146	101
Chloral	246	302	382	227	155
Tanning	798	1,549	567	484	510
Chemicals, soap, artificial silk, etc	11,381	6,905	6,770	6,865	10,400
Scientific uses	519	864	1,193	2,457	1,302
Ether, fulminates, and explosives	63,879	89,917	112,121	128,954	146,572
Total hectoliters	374,598	423,561	472,239	545,467	593,836

This shows a total denaturation in 1907 of 15,689,246 gallons. It thus appears that the increased consumption of denatured alcohol in France is due almost entirely to two groups of uses, namely, for heating and lighting purposes, and for the manufacture of ether and explosives.

The use of alcohol as fuel for motors has not yet attained in France the importance that was anticipated when the internal-revenue tax was reduced to a merely nominal rate of 5 cents per hectoliter in 1901, because of the high cost of denaturing materials, the tendency of alcohol vapor when burned to corrode the interior of cylinders, and the fact that alcohol, without a large admixture of benzol or gasoline, does not explode with sufficient rapidity to meet the requirements of automobile practice, and requires to be used in motors with valves and ignition apparatus specially adapted to that purpose.

The cost of denatured spirits fluctuates naturally in France as elsewhere with the wholesale market value of pure alcohol, which has ranged during the past year from 47.6 francs ($9.18) per hectoliter in June last, to 44 francs ($8.49), which was the mean price for first quality, 90° spirit (not including the entrepôt tax of 39 cents per hectoliter) in the wholesale market of Paris during the week ended October 17th.

The alcohol used for denaturation is generally of the second and third qualities, and the open-market values of denatured spirits in Paris on October 27th were as follows: First quality, 55 francs per hectoliter, or $10.61 per 26½ gallons; second quality, 42 francs, or $8.10. The retail price was 0.65 franc per liter, or $0.47 per gallon.

Paris imposes no *octroi* tax upon denatured alcohol, whereas alcohol of 60°, not denatured, is subject on entry into the city to a municipal tax of 2.79 francs, or 53 cents, per liter.—*Daily Consular Report*, Nov. 30, 1908.

Consul James G. Carter makes the report from Tamatave that petroleum has been recently discovered in Madagascar, the particulars being as follows:

The oil occurs in the nature of several springs which occur in the regions of the Manambolo and Manamboa rivers, on the west coast of the island, and while there has not yet been any official announcement of concessions being granted for oil prospecting, I have been reliably informed that there are several concession holders [names and addresses are obtainable from the Bureau of Manufactures]. Thus far no serious work has been done on the fields, but it is believed that extensive operations will commence shortly.

According to a local newspaper, a colonist residing in the environs of Tullear, on the southwest coast of Madagascar, has recently shipped to the governor-general at Tananarive a sample block of 60 kilos (132 pounds) of coal, said to have been taken from existing coal deposits found in the regions of Tullear.—*Daily Consular Report*, Dec. 5, 1908.

Japanese Camphor Trade.

Consul John H. Snodgrass writes from Kobe that for the period from January to September, 1908, there was an appreciable decrease in the exports of camphor from Japan, they being reduced to 1,934,000 pounds, valued at $844,500 and 760,000 pounds of camphor oil, worth $53,500. The details follow:

The following table shows the amount and value of camphor exports for the first eight months of 1906, 1907, and 1908:

	1906.	1907.	1908.
Pounds	2,453,334	3,236,667	1,938,000
Value	$1,140,000	$2,030,000	$844,500

On May 1, 1907, the market price was 140 yen per 100 kins ($70 per 132.51 pounds), and refined camphor was 220 to 230 yen ($110 to $115), but the ruling price has gone down as low as one-third of that of 1907, and yet the demand abroad is not brisk. The monopoly bureau has lowered the price to 80 yen ($40), but stocks are plentiful and the market price is gradually decreasing, causing a number of dealers to close up business. One of the reasons offered for the loss of this foreign trade is the keen competition caused by the introduction of German artificial camphor and the entrance of China into the lists for supplying the natural product.—*Daily Consular Report*, Dec. 12, 1908.

Zinc Mining in Mexico.

Working and Output of the Mines in the State of Chihuahua.—In compliance with instructions, Consul Louis A. Martin, with the coöperation of H. B. Pulsifer, mining expert, has prepared the following report covering the zinc mine industry of Chihuahua:

Zinc ore bodies are found in the following camps in the State of Chihuahua: (1) Picachos, on the Kansas City, Mexico and Orient Railroad, less than 100 miles from Presidio del Norte, opposite the Texas border, where carbonate ores are mainly produced, sulphides occurring, but not on a commercial scale; (2) Santa Eulalia, near the city of Chihuahua, produces carbonate ore exclusively; (3) near San Ysidro, on the Chihuahua and Pacific Railroad, where sulphides only are produced; (4) Almoloya, where carbonate and silicate are produced, and Parral and Santa Barbara, producing sulphides only.

The zinc ore bodies are found associated with silver-lead mines, and in this way partake of the development of the latter, although certain mines might properly be called zinc mines. In every case, however, silver-lead ores are those sought for and mined. A conservative estimate places the crude zinc-bearing ores, more or less well exposed, in the State at 1,000,000 tons, *viz.*, Picacho, 50,000 tons; Santa Eulalia, 100,000 tons; San Ysidro, 200,000 tons; Almoloya, 50,000 tons; Parral and Santa Barbara, 600,000 tons. The probable available amount is many times this, most of the present mining being at very moderate depths.

The carbonate and silicate ores are running from 32 to 45 per cent. metallic zinc, as broken off, after the merest hand sorting. Crude sulphide ores will run from 10 to 35 per cent. metallic zinc. The carbonate ores always carry a trifling amount of silicate, sometimes a little lead carbonate, calcium carbonate, and iron minerals.

Disposition of Sulphide.—The sulphide ores are always complex and must, as at present disposed of, be milled. A silver-lead concentrate, possibly carrying some iron and gold, is the marketable product always procurable at the same time as the zinc concentrate.

The mines are in all possible conditions of development, from the simplest tunnel adit, where the ore is found at or above the tunnel level and is simply broken down, run through chutes into the mine car, and pushed to the open, to where the ore is found at moderate depths, 100 to 400 feet, and reached by shafts and drifts or by tunnels and internal hoists. Ore is seldom found at considerable depths, as at 1,600 feet, but in such case it is reached by high-speed first-motion hoists. This special case is in a very large and rich silver-lead mine, where the zinc ore may be said to be a valuable by-product.

A considerable part of the ore is mined by hand drilling, but power drills, worked by compressed air from steam or gas engines, supplied with producer gas, are used in the larger mines and will supplant hand drilling as the mines become developed.

Sulphide ores present hard and complex milling difficulties. Formerly zinc ores were a detriment to sulphide ores. The ores being valued for the silver-lead content and disposed of to the smelters without removing the zinc, were not only losing their zinc value, but were penalized for its presence; but from a detriment it is now changed to a valuable product, consequent on the art of separating and utilizing the zinc portion. Mines equally rich as those worked are found idle and unequipped in developing plants, owing to local conditions and management.

Even during these times of unusual depression in the metal market, experiments on a large scale are in progress at several of the mines, and the future industrial development will surely be of great magnitude.

Cost of Production.—The question of the cost of production of zinc ore presents certain complications from the fact that the ore occurs with other valuable ores, as at Santa Eulalia, or that other valuable products are obtained at the same time, as at the mine near San Ysidro, or from the fact that nearly all the mines are at present working much under normal capacity.

At Picachos the case is simple; zinc ore alone is produced, and practically all the cost is that of labor. The total cost (mining and hauling to points in Kansas) should not exceed $12.32 (American currency, which is the unit used throughout this report) per ton.

From the mine near San Ysidro, where mining cost is very low, where 45 per cent. zinc is produced from zinc concentrate, with silver-lead concentrate, the total cost (mining, handling, freightage, etc., to points in Kansas) should not be much more than $13.57 per ton.

In Santa Eulalia the cost of production is also very low, and the total cost, laid down at points in Kansas, should not exceed $9.75 per ton.

The foregoing mines are producing almost the whole amount now being shipped from the State of Chihuahua, which for September and October was about 125 tons per day.

From Picachos comes carbonate, lead-free, 45 per cent. of zinc; from San Ysidro, sulphide concentrate, 45 per cent. of zinc; from Santa Eulalia, carbonate, lead-free, 35 per cent. of zinc.

As far as known, there are no facilities for smelting zinc ores in Mexico. Coal and wood, the chief fuels in Chihuahua, are too expensive, the wholesale prices being as follows per ton: Coal, $6 to $8; wood, $3 to $5. The production of zinc ore and concentrates is a new industrial development, and, so far as known, the product is shipped to the United States exclusively.—*Daily Consular Report*, Dec. 7, 1908.

Responding to a New York inquiry in regard to the new patent act in the United Kingdom, Consul J. N. McCunn writes from Glasgow, as follows:

With regard to the clause "to an adequate extent," I am informed that it would appear to be perfectly in order, in the meantime, to manufacture the parts of a machine in the United States and have them assembled in the United Kingdom. The ground on which this view is taken is that each part of the machine, taken separately, is not a patented article, the patent merely applying to the machine as a whole. No test case has yet been taken in the British courts, and I am informed that the above is the generally accepted reading of the law until such a test case is brought.

A company has recently been started in Glasgow having for its object the safeguarding of the property of foreign patentees selling in the British Isles, and one of their pamphlets, which gives excerpts from the patent act, is forwarded and may be obtained from the Bureau of Manufactures.—*Daily Consular Report*, Dec. 14, 1908.

(It is understood that the British Patent authorities do not agree with the opinion expressed above, but take the contrary view.—Ed.)

Consul-General Robert P. Skinner, of Hamburg, writes under date of November 16th, that very little refined and

caustic potash had been used during the previous few months and that the market was comparatively lifeless, to which he adds:

There is now some improvement, inquiries are coming in, and for 1909 contracts have been closed at higher prices. Refined potash is quoted to-day, per 100 kilos (220 pounds), as follows: 80 to 85 per cent. goods, 32 marks ($7.62); 90 to 92 per cent. goods, 34.5 marks ($8.21), including original barrels of 500 kilos (1,100 pounds), f. o. b. Hamburg. Net cash fo lots of 5,000 kilos (5 tons).

Caustic potash of non-German origin is quoted to-day, per 100 kilos: 70 to 72 per cent. goods, 45 francs ($8.68); 74 to 76 per cent. goods, 47.5 francs ($9.17); 80 to 85 per cent. goods, 51.5 francs ($9.94), including drums, containing about 250 kilos (550 pounds), f. o. b. Antwerp. Cash less 2 per cent. discount by orders of 5,000 kilos (5 tons).

The exports of potash from Hamburg in 1906 were 6,276 tons, valued at $496,449, and in 1907, 7,436 tons, valued at $588,029.

(The exports of chloride of potassium from all Germany in 1907 amounted to $5,995,934, of which a large share is shipped to the United States.—B. of M.).—*Daily Consular Report*, Dec. 19, 1908.

Niagara Power Distribution.—Consul Harry A. Conant, of Windsor, sends the following account of the present status of the distribution in Canada of electric power from Niagara Falls:

An assurance that Windsor can secure Niagara power under the Ontario government scheme for about half the cost of production by coal and for at least $5 a horse-power less than Toronto corporations are paying the Electrical Development Company for power from the falls, was given by Hon. Adam Beck, minister of power in the Ontario cabinet, in discussing the government power proposition at a public meeting held in Windsor, December 1st.

In addition to paying the actual cost of $9 or $9.40 a horse-power at the falls, municipalities will be required to pay operating expenses, besides 4 per cent. of the actual cost of construction transmission lines, and a sinking fund sufficient to wipe out the cost of construction in thirty years, each municipality being assessed its share.

One point on which Mr. Beck laid emphasis is that the rates to be charged by the city after purchasing power from the government commission are subject to regulation by the commission. The municipality can not sell for less than cost, and it is thus prevented from bonusing industries by offering free power, while a protest from any rate payer who believes the rate is too high will be sufficient to insure an arbitration by the commission.

Work on the western extension of the transmission line can be carried on while the building of the line already contracted for is under way. In that case the line to Windsor ought to be finished in little more than a year.—*Daily Consular Report*, Jan. 5, 1909.

Sulphur in Chile. Consul Rea Hanna, of Iquique, in response to a California inquiry, has secured from a firm in Chile information in regard to the deposits and refining of sulphur in Chile. The agent of the refinery at Tacna writes as follows

As to the advisability of securing crude native sulphur in Tacna and its neighborhood and shipping same to the United States for refinement or to be used there, the crude sulphur is never sent to Tacna, nor yet is it made up for exportation, as the danger is that in the crude state there is a foreign matter that would burn any class of sack in which it might be shipped.

The two classes of sulphur to be secured in this district are: (1) Azufre sublimado or flour sulphur of a ley of 99.82 and 75°; (2) refined sulphur in lumps of a ley of 99½. The price of the former is $6.30 Chilean (at 18 pence exchange = $2.2995 American gold) per quintal (101.61 pounds) and the refined at $4.30 ($1.5695 American gold). Both these prices are cash down for the goods placed in the railway station at Tacna. To insure a general all-round supply contracts must be made and a few commissions allowed.

There is already some scheme to secure the whole production, but we are without full details. From one source a supply of 500 quintals monthly can be contracted, and this can be easily doubled should the business appear feasible, on the terms indicated.—*Daily Consular Report*, Jan. 9, 1909.

Consul Maxwell Blake, of Dunfermline, writes that approximately 1,500 tons of acetone, valued at about half a million dollars, are annually consumed in Great Britain, practically all of which is imported from the United States. His details of this trade follow:

There seems to be but one company manufacturing this article in Great Britain. By far the larger percentage of this import is utilized as the solvent ingredient of smokeless powder, guncotton, and mine explosives; but it is also employed in the making of chloroform, for the preparation of photographic sensitive plates, and as a valuable constituent of certain dyes.

Up to the present time all efforts on the part of the British Government, as well as of various private chemical concerns in this country, have utterly failed to provide acetone in quantities sufficient to supply the commercial demand for it. It is now stated, however, that a simplified method of wood distillation lately discovered and put in practice by a certain French chemist, has gone far toward successfully cheapening its production, it being now successfully manufactured as a by-product of charcoal. In consequence of this, Great Britain expects to look more to France than formerly as a source of supply for this product. A technical description of this new French method of wood distillation, which is also likely to soon be imitated by British manufacturers of this product, can easily be procured.—*Daily Consular Report*, Jan. 15, 1909.

Recently Representative Hull introduced a bill into Congress, the purpose of which is to regulate interstate commerce of misbranded products of all kinds. As considerable opposition has developed, the bill will probably remain with the committee.

A bill for the taxation of bay rum from Porto Rico on the same basis with other products from the island has been introduced into Congress by Chairman Payne.

The Mann bill introduced into the House last spring, will

come up for action in the Committee on Interstate and Foreign Commerce shortly. This measure is strenuously opposed by the National Wholesale Drug Association, the Proprietary Association of America and the National Association of Retail Pharmacists. This bill not only prohibits the sale of all narcotics, their derivatives and preparations except on the prescription of a physician, dentist or veterinarian. It also compels that a poison label be placed on all preparations containing even an infinitesimal amount of such oils as pennyroyal, and bitter-almonds, salts of copper, lead, silver, zinc, hydroxides of the alkalies and concentrated mineral acids.

In the suit to dissolve the Standard Oil Company, of New Jersey, before Special Examiner Franklin Ferris, Mr. W. W. Tarbell testified on January 13th that the United States Pipe Line Company, a Standard competitor, is now and has for several years been operating as a common carrier under the laws of Pennsylvania Mr. Tarbell is general manager of the United States Pipe Line Co. and Pure Oil Co.

In the United States District Court at Chicago, on January 13th, one of the most important patent litigations of recent years was started by the Union Carbide Company, of New York, against the American Carbolite Company, of Duluth. The Union Carbide Company is capitalized at $14,000,000 and has factories at Niagara Falls and Sault Ste. Marie and owns numerous patents on the production of calcium carbide and processes of manufacture. The charge against the Duluth Company is an infringement of the fundamental patent, in addition to damage sustained by the Union Carbide Company in sale and use of this product and perpetual injunction is asked.

Mr. Geo. O. Knapp is president and Mr. W. P. Martin, vice-president of the Union Carbide Company. The directors are C. K. G. Billings, A. N. Brady, E. N. Dickerson and C. F. Deiterich; A. B. Proal is treasurer. The American Carbolite Company started to manufacture and sell carbide over a year ago. Suits against the company have previously been started in New York and Ohio courts.

The demands made in the bill filed in the present instance are: that the American Carbolite Company be enjoined perpetually from using crystalline calcium carbide in any way; that it be forced to appear in court and give an account of the profits derived from such use of the patent; that it be forced to pay damages to the Union Carbide Company; that the material on hand in the plants of the American Carbolite Company be destroyed; and that the defendant pay the costs of the suit.

It is set forth in the bill that calcium carbide was discovered by Thomas Willson, an electrical engineer, through experiments in his laboratory in Spray, N. C., in 1892. The manner of the discovery is set forth in a report of the department of chemistry of the University of Pennsylvania as follows:

"Mr. Willson was conducting experiments with a view to the preparation of metallic calcium, for which purpose he employed an improved Héroult electric furnace with a current of 2,000 amperes and 36 volts, operating upon a mixture of lime and coal-tar. He secured a melted mass of dark color, which on cooling became solid and brittle. This product was thrown into a neighboring stream as useless, when to the astonishment of those who saw it, there was liberated suddenly a great quantity of gas which on being kindled, burned with the now familiar bright but smoky flame, and gave off quantities of soot which showed that it was a rich hydrocarbon gas. The smelt was repeated, the product submitted to analysis, which demonstrated that the solid substance contained calcium carbide and that the gas was acetylene."

In June, 1895, it is declared in the bill, Mr. Willson obtained a patent from the United States government upon crystalline calcium carbide, the patent dating June 18, 1895, and running for seventeen years.

August 24, 1903, it is further declared this patent was sold to the Union Carbide Company. The process, however, was an open one, and a year ago the American Carbolite Company started up with this patent as a basis of its manufactures, according to the bill. Several warnings have been issued by the Union Carbide Company to all concerns engaged in the manufacture and sale of the carbide, but the American Carbolite Company, it is said, has refused to heed these warnings and has threatened to go ahead. The bill was filed by the firm of Offield, Towle and Linthicum.

The United States Geological Survey has issued the following letter and circular which are self-explanatory.

DEPARTMENT OF THE INTERIOR UNITED STATES GEOLOGICAL SURVEY, WASHINGTON.

Office of the Director. January 9, 1909.

SIR:

A series of preliminary tests of explosives in the presence of coal dust, inflammable gas, etc., has now been completed at the United States Geological Survey testing station at Pittsburg, Pa., and in the course of a few days this Survey will be ready to begin official tests of explosives which the manufacturers thereof may desire to have tested as to their permissibility for use in mines containing gas, gas and dust, or dust in dangerous quantities.

I enclose herewith a statement of the test requirements to which the various explosives manufactured for use in such mines will be subjected at this station. The conditions under which these tests are to be made are as follows:

(1) The manufacturer is to furnish 100 pounds of each explosive which he desires to have tested; he is to be responsible for the care, handling, and delivery of this material at the testing station on the United States Arsenal grounds, Fortieth and Butler Streets, Pittsburg, Pa., at the time the explosive is to be tested; and he is to have a representative present during the tests who will be responsible for the handling of the packages containing the explosives until they are opened for testing.

(2) No one is to be present at or to participate in these tests except the necessary Government officers at the testing station, their assistants, and the representative of the manufacturer of the explosives to be tested.

(3) The tests will be made in the order of the receipt of the applications for them, provided the necessary quantity of the explosive is delivered at the plant by the time assigned, of which due notice will be given by the Geological Survey.

(4) Preference will be given to the testing of explosives that are now being manufactured and that are in that sense already on the market. No test will be made of any new ex-

plosives which is not now being manufactured and marketed, until all explosives now on the market that may be offered for test have been tested.

(5) A list of the explosives which pass certain requirements satisfactorily will be furnished to the state mine inspectors, and will be made public in such further manner as may be considered desirable.

If you are manufacturing any explosive which you desire to have tested under the conditions specified above, please notify this office to that effect and, at the same time, send a copy of your communication to Mr. J. C. Roberts, U. S. Geological Survey, Fortieth and Butler Streets, Pittsburg, Pa.

It is expected that subsequent to the completion of these tests of explosives for the manufacturers, the station will also make tests of these explosives as they are supplied for use in coal mines in the various states.

Very respectfully,
GEO. OTIS SMITH,
Director.

DEPARTMENT OF THE INTERIOR, UNITED STATES GEOLOGICAL SURVEY.

Test Requirements for Explosives Used in Coal Mining.

The tests will be made by the engineers of the United States explosives testing station at Pittsburg, Pa., in gas and dust gallery No. 1. The charge of explosive, to be fired in tests 1 and 2, shall be equal in disruptive power to one-half pound of nitroglycerine dynamite in its original wrapper, of the following formula:

	Per cent.
Nitroglycerine	40
Nitrate of sodium	44
Wood pulp	15
Calcium carbonate	1
	100

Each shot shall be fired with an electric fuse of sufficient power to completely detonate or explode the charge, as recommended by the manufacturer. The explosives must be in such condition that the chemical and physical tests do not show any unfavorable results. The explosives in which the charge used is less than 100 grams will be weighed in tin foil without the original wrapper.

The dust used in tests 2, 3, 4, and 5, will be of same degree of fineness and taken from one mine.

Test 1.—Ten shots with a charge as described above, in the original wrapper, shall be fired, each with 1 pound of clay tamping, at a gallery temperature of 77° Fahrenheit, into a mixture of gas and air containing 8 per cent. of methane and ethane. An explosive will pass this test if all ten shots fail to ignite the mixture.

Test 2.—Ten shots with charge as previously noted, in its original wrapper, shall be fired, each with 1 pound of clay tamping at a gallery temperature of 77° Fahrenheit, into a mixture of gas and air containing 4 per cent. of methane and ethane and 20 pounds of coal dust, 18 pounds of which is to be placed on shelves laterally arranged along the first 20 feet of the gallery, and 2 pounds to be placed near the inlet of the mining system in such a manner that all or part of it will become suspended in the first division of the gallery. An explosive will pass this test if all ten shots fail to ignite the mixture.

Test 3.—Ten shots with charge as previously noted, in its original wrapper, shall be fired, each with 1 pound of clay tamping at a gallery temperature of 77° Fahrenheit, into 40 pounds of bituminous coal dust, 20 pounds of which is to be distributed uniformly on a horse placed in front of the cannon and 20 pounds placed on side shelves in sections 4, 5 and 6. An explosive will pass this test if all ten shots fail to ignite the mixture.

Test 4.—A limit charge will be determined within 25 grams by firing charges in their original wrappers unstemmed at a gallery temperature of 77° Fahrenheit, into a mixture of gas and air containing 4 per cent. of methane and ethane and 20 pounds of bituminous coal dust, to be arranged in the same manner as in test 2. This limit charge is to be repeated five times under the same conditions before being established.

Test 5.—A limit charge will be determined under the same conditions as in test 4, except that 2 per cent. of methane and ethane will be used instead of 4 per cent.

Note.—At least 2 pounds of clay stemming will be used with slow-burning explosives.

WASHINGTON, D. C.,
January 8, 1909.

OFFICIAL REGULATIONS AND RULINGS.

FOOD INSPECTION DECISION 98.

The Labeling of Whiskey Compounds.—The labeling of whiskey compounds, under the Food and Drugs Act of June 30, 1906, will be governed by the opinion of the Attorney-General, dated December 1, 1908, published herewith.

(Signed) JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *December 4, 1908.*

DECEMBER 1, 1908.

The Honorable, the Secretary of Agriculture.

SIR: I am duly in receipt of your letter of this date. In this you call my attention to a passage in my opinion of April 10, 1907, addressed to the President, which passage is in the words following:

I conclude that a combination of whiskey with ethyl alcohol, supposing, of course, that there is enough whiskey in it to make it a *real* compound and not a mere semblance of one, may be fairly called "Whiskey," provided the name is accompanied by the word "Compound" or "Compounded," and provided a statement of the presence of another spirit is included in substance in the title—and you ask me how much whiskey there must be in a mixture of whiskey and neutral spirits to fairly entitle this mixture to be called a "Compound" or "Compounded" whiskey, or, as stated in your letter, "whiskey: a compound of pure grain distillates."

In the passage in question I stated that there must be, in any such a mixture, "enough whiskey * * * to make it a *real* compound and not a mere semblance of one." In the absence of any legislative provision or judicial determination on this subject, the proportion of whiskey necessary for the purpose in question can be stated only tentatively and for the time being; and a selection of any particular fraction of the whole as a necessary proportion must be, at least in appearance, somewhat arbitrary. I have, however, very carefully examined the evidence on this subject,

submitted by your department, and, after full consideration of such evidence, have reached the conclusion that, until better informed in the premises from the action of the Congress or of the courts, this department will not advise a prosecution on the ground of violation of law in using any one of the three labels above suggested or any substantial equivalent therefor when the amount of whiskey in the mixture equals or exceeds one-third in volume of the spirituous content; that is to say, in the case you mention, one-third of the whiskey and neutral spirits combined.

Very respectfully,

CHARLES J. BONAPARTE,
Attorney-General.

FOOD INSPECTION DECISION 99.

Change in Form of Guaranty Legend. (Amending Section *b* of Regulation 9).—Section 9 of the Food and Drugs Act, June 30, 1906, provides that no dealer shall be prosecuted under the provisions of the act when he can establish a guaranty signed by the wholesaler, jobber, manufacturer, or other party residing in the United States, from whom he purchases such articles, to the effect that the same are not adulterated or misbranded within the meaning of the act. There is a further provision that the guarantor shall, if the goods be adulterated or misbranded within the meaning of the act, be amenable to the prosecutions, fines, and other penalties which would attach in due course to the dealer.

Section *b* of Regulation 9 provides that a general guaranty may be filed with the Secretary of Agriculture by the manufacturer or dealer and be given a serial number, which number should appear on each and every package of goods sold under such guaranty, with the words "Guaranteed under the food and drugs act, June 30, 1906."

It is obvious from a reading of Section 9 of the act that the guaranty is in no sense a guaranty by the Government, and that it is merely an assumption of responsibility for the character or labeling of the goods by the manufacturer, jobber, or packer. Yet, notwithstanding this plain fact, attempts have been made by some unscrupulous persons to cause the public to interpret the phrase "Guaranteed under the food and drugs act, June 30, 1906," as a guaranty by the government that the goods upon which the phrase appears are pure and conform, in all respects, with the provisions of the act. This misrepresentation has been scattered broadcast in prominent advertisements in the press, and by means of circulars and billboard posters. Even in the absence of such misrepresentation there can be no doubt that the phrase, unfortunately, is misleading, and is therefore prohibited by the law and should be changed. The Commissioner of Patents has refused to register trade-marks of which the phrase formed a part, on the ground that it is misleading and under the law can not be registered. The Board of Food and Drug Inspection for some time has realized that the wording of the guaranty legend should be changed, but it has also been mindful of the fact that the manufacturers and jobbers of the United States have, in the aggregate, large sums of money invested in labels and plates, upon which appears the legend in its present form, a form indorsed by the regulations and copied therefrom in good faith by the owners of these labels and plates. Entirely apart from the expense and loss of property, it is a fact that a change in the form of the legend, without due notice, would seriously embarrass business interests, because the printing and lithographing of new labels will require considerable time.

As a solution of the question, the Board recommends that the guaranty legend be changed so as to show plainly that the guaranty is that of the manufacturer and not of the government, that the old form of labels now in use representing guaranties already filed with the Department of Agriculture shall be recognized for a term of two years, and that for all guaranties filed with the Department of Agriculture on and after January 1, 1909, the guaranty legend shall read "Guaranteed by [insert name of guarantor] under the food and drugs act, June 30, 1906."

Accordingly, the following amendment is proposed to Regulation 9 of the Rules and Regulations for the Enforcement of the Food and Drugs Act:

Section *b* of Regulation 9 is hereby amended to read as follows:

(*b*) A general guaranty may be filed with the Secretary of Agriculture by the manufacturer or dealer and be given a serial number, which number shall appear on each and every package of goods sold under such guaranty with the words "Guaranteed by [insert name of guarantor] under the food and drugs act, June 30, 1906."

This amendment shall become and be effective on and after January 1, 1909. Labels bearing the form of guaranty legend provided in the original regulations and representing guarantees now on file with the Department of Agriculture may be used for a period of two years, but it is suggested that, as new labels are prepared, the change in the form of guaranty legend should be made.

H. W. WILEY,
F. L. DUNLAP,
GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved:

GEO. B. CORTELYOU,
Secretary of the Treasury,
JAMES WILSON,
Secretary of Agriculture,
OSCAR S. STRAUS,
Secretary of Commerce and Labor.

WASHINGTON, D. C., *December 8, 1908.*

FOOD INSPECTION DECISION 100.

Bleached Flour.—Flour bleached with nitrogen peroxide, as affected by the Food and Drugs Act of June 30, 1906, has been made the subject of a careful investigation extending over several months.

A public hearing on this subject was held by the Secretary of Agriculture and the Board of Food and Drug Inspection, beginning November 18, 1908, and continuing five days. At the hearing those who favored the bleaching process and those who opposed it were given equal opportunities to be heard.

It is my opinion, based upon all the testimony given at the hearing, upon the reports of those who have investigated the subject, upon the literature, and upon the unanimous opinion of the Board of Food and Drug Inspection, that flour bleached by nitrogen peroxide is an adulterated product under the Food and Drugs Act of June 30, 1906; that the character of the adulteration is such that no statement upon the label will bring bleached flour within the law; and that such flour can not legally be made or sold in the

District of Columbia or in the Territories; or be transported or sold in interstate commerce; or be transported or sold in foreign commerce except under that portion of Section 2 of the law which reads:

* * * *Provided*, That no article shall be deemed misbranded or adulterated within the provisions of this act when intended for export to any foreign country and prepared or packed according for the specifications or directions of the foreign purchaser, when no substance is used in the preparation or packing thereof in conflict with the laws of the foreign country to which said article is intended to be shipped: * * *

In view of the extent of the bleaching process and of the immense quantity of bleached flour now on hand or in process of manufacture, no prosecutions will be recommended by this Department for manufacture and sale thereof in the District of Columbia or the Territories or for transportation or sale in interstate or foreign commerce, for a period of six months from the date thereof.

JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *December 9, 1908.*

FOOD INSPECTION DECISION 101.

Benzoate of Soda.—Frequent inquiries have been received by the Department in regard to the use of benzoate of soda in foods. The following is typical of this class of inquiries:

In F. I. D. 89, the position of the National authorities in regard to the use of benzoate of soda is to allow its use in food, pending the report of the Referee Board of Consulting Scientific Experts. Based upon Bulletin 84, Part IV, of the Bureau of Chemistry, issued subsequent to F. I. D. 89, certain manufacturers of food products are representing to the officials of the States, charged with the enforcement of food laws, and to the consuming public generally, that the U. S. Government has condemned the use of benzoate in foods. We write to ask the position of the Deparment on this subject.

The Department has not changed the position outlined in Food Inspection Decision 89. Pending the determination by the Referee Board of the wholesomeness or unwholesomeness of benzoate of soda, its use will be allowed under the following restrictions:

Benzoate of soda, in quantities not exceeding one-tenth of one per cent., may be added to those foods in which, generally heretofore, it has been used.

The addition of benzoate of soda shall be plainly stated upon the label of each package of such food.

F. L. DUNLAP,
GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved:
JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *December 18, 1908.*

FOOD INSPECTION DECISION 102.

Entry of Vegetables Greened with Copper Salts.—Until further notice, vegetables greened with copper salts, but which do not contain an excessive amount of copper and which are otherwise suitable for food, will be allowed entry into the United States, if the label bears the statement that sulphate of copper or other copper salts have been used to color the vegetables.

Food Inspection Decision No. 92 is amended accordingly.

GEO. B. CORTELYOU,
Secretary of the Treasury.
JAMES WILSON,
Secretary of Agriculture.
OSCAR S. STRAUSS,
Secretary of Commerce and Labor.

WASHINGTON, D. C., *December 23, 1908..*

Under date of October 10, 1908, the Board of Food and Drugs Inspection has announced the following judgments under the Food and Drugs Act: No. 12, Misbranding of Flour (hard spring wheat mixed with durum); No. 13, Misbranding of Flour (as to place and manner of manufacture); No. 14, Misbranding of Vanilla Extract (imitation colored with caramel); No. 15, Adulteration and Misbranding of Whiskey (neutral spirits artificially colored); No. 16, Misbranding of a Drug Product (Sartoin skin food); No. 17, Misbranding of Flour (as to place of manufacture and name of manufacturer).

Under date of October 2nd, judgments Nos. 18–21, all concerning the Misbranding and Adulteration of Honey, Glucose and Invert Sugar being present.

Under date of November 25th, judgment No. 25, Misbranding of a Drug (Harper's Cuforhedake Brane Fude or Cuforhedake Brain Food).

Under date of Nov. 16th, Nos. 26–27, Misbranding of Canned Blackberries.

Under date of December 28th, the following: No. 28, Adulteration and Misbranding of Pepper; No. 29, Misbranding of a Drug Product (Liquid Sulphur); No. 30, Misbranding of a Drug Product (Concentrated Oil of Pine Compound); No. 31, Adulteration and Misbranding of Buckwheat Flour; No. 32, Misbranding of a Drug Product (Blackburn's Cascara, Wild Lemon, Castor Oil Pills, Compound); No. 33, Misbranding of Maple Sirup; Nos. 34 and 35, Misbranding of Canned Peaches.

(T. D. 29342). Nov. 11, 1908.—Countervailing duty on wood pulp and other products of wood imported from Sweden.

(T. D. 29343). Nov. 14, 1908.—Drawback on leather manufactured by Thomas A. Kelley & Co., of West Lynn, Mass., with the use of imported bichromate of soda, logwood crystals and refined glycerin.

(T. D. 1433). Nov. 13, 1908.—Bottling of spirits in bond. No foreign materials such as caramel or rock candy sirup to be added.

(T. D. 1434). Nov. 16, 1908.—Compound known as Marrofat exempt from taxation as a substitute, not being made in imitation or semblance of butter or calculated or intended to be sold as butter.

(T. D. 1435). Nov. 16, 1908.—Suspension of the provision of regulations prohibiting use of fortified wines in the manufacture or preparation of patent or proprietary medicines or compounds.

(T. D. 1436). Nov. 17, 1908.—Record of grape brandy.

(T. D. 29354). Nov. 21, 1908.—When apparatus, imported free of duty for a scientific or educational institution under paragraph 638, tariff act of 1897, is rejected for any reason by such institution, rejection should be reported to the collector of customs at port of entry in order that duties may be collected.

(T. D. 29356). Nov. 23, 1908.—Drawback on Giant Dynamite Powder, in cartridge form, manufactured by the Giant Powder Company, Consolidated, of San Francisco, Cal., in part with the use of imported wood flour. T. D. 27138 of February 20, 1906, extended.

(T. D. 1437). Nov. 21, 1908.—Rectifiers prohibited from making a so-called wine mash and using the product thereof in the production of compound liquors.

(T. D. 29365). Nov. 25, 1908.—Drawback on steel rails manufactured by the Bethlehem Steel Company, of South Bethlehem, Pa., with the use of imported iron ore. T. D. 27127 of February 19, 1906, extended.

(T. D. 29370–G. A. 6830). Nov. 25, 1908.—Gauge of oil. Dutiable quantity-method of ascertainment. In ascertaining the value of oil dutiable on an *ad valorem* basis, it is proper to ascertain in American gallons the quantity actually arriving in this country, and afterwards to reduce the unit of the invoice to English or imperial gallons in the relative ratio of 231 cubic inches for the American gallon, liquid measure, and 277.274 cubic inches for the English gallon. The proper value would thus be determined by multiplying the number of gallons by the price per gallon, as shown by the invoice, if found to be correct by the appraiser.

(T. D. 29373). Nov. 17, 1908.—Court decision adverse to the government. Petroleum products countervailing duty-Belgian paraffin. Paraffin which is derived from petroleum originating in Russia, a country that imposes a duty on petroleum products exported from the United States, but which is manufactured in Belgium, a country that imposes no such duty, is not subject to the countervailing duty provided in paragraph 626, tariff act of 1897, on "the products of crude petroleum produced in any country, which imposes a duty on petroleum or its products exported from the United States."

(T. D. 29374). Nov. 16, 1908.—Decision adverse to the government. Casein-lactarene. Casein is free of duty as "lactarene," under paragraph 594, tariff act of 1897.

(T. D. 1438). Nov. 23, 1908.—Certification, by collectors, of specially denatured alcohol used or disposed of by manufacturers or dealers during the month.

(T. D. 1439). Denatured alcohol. Authorizing formula 17 as special denaturant for use in the manufacture of chloral hydrate.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., November 24, 1908.

SIR: You will please inform the ———, in your district, that the following formula has been authorized as a special denaturant for use in the manufacture of chloral hydrate:

Formula 17.—To 100 gallons of ethyl alcohol add 0.05 gallon (6 ½ fluid ounces) of animal oil.

The animal oil must conform to the following specifications:

Color.—The color shall be a deep brown.

Boiling Point.—When 100 cc. of the animal oil are subjected to distillation in the same manner as prescribed for the determination of wood alcohol in Section 26, Part I of the Regulations, not more than 5 cc. should distil over below 90° C., and not less than 50 cc. at 180° C.

Pyrrol Reaction.—Two and one-half cc. of a 1 per cent. solution of the animal oil in 90 per cent. alcohol are diluted to 100 cc. with alcohol. A splinter of pine wood, previously moistened with concentrated hydrochloric acid, is dipped into 10 cc. of this solution, containing 0.025 per cent. of animal oil. After a few minutes, the splinter should show a distinct red coloration.

Reaction with Mercuric Chloride.—Five cc. of the 1 per cent. solution of the animal oil in 90 per cent. alcohol, when treated with 5 cc. of a 2 per cent. solution of mercuric chloride in alcohol should give immediately a voluminous flocculent precipitate. Five cc. of the 0.025 solution of the animal oil when treated with 5 cc. of the 2 per cent. solution of mercuric chloride, should show at once a distinct turbidity.

Respectfully,
ROBT. WILLIAMS, JR.,
Acting Commissioner.

MR. E. B. ALLEN, *Collector First District, St. Louis, Mo.*

(T. D. 1440). Denatured alcohol. Authorizing formula 1 as special denaturant for use in the manufacture of furniture polish.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., November 28, 1908.

SIR: You are informed that formula 1 (to 100 gallons of ethyl alcohol add 5 gallons of approved wood alcohol) has been authorized as a special denaturant for use in the manufacture of furniture polish.

Applicants for a permit for the use of this formula in this line of manufacture must forward to this office the formula for the furniture polish they propose to make, together with a sample of the same, the sample to consist of not less than 1 pint.

Respectfully,
ROBT. WILLIAMS, JR.,
Acting Commissioner.

MR. W. V. MCMAKEN, *Collector Tenth District, Toledo, O*

(T. D. 29388—G. A. 6833). Dec. 8, 1908.—Olive oil—"fit only." Olive oil which, although imported in good faith for manufacturing or mechanical purposes and actually used for such purposes, is of a grade that is suitable for human consumption as food, is not within the provision in paragraph 626 of the free list of the tariff act of 1897, for "olive oil for manufacturing or mechanical purposes fit only for such use," but is subject to duty under paragraph 40, relating to "olive oil, not specially provided for."

(T. D. 29425—G. A. 6838). Sugar—polariscopic tests—Regulations of the Secretary of the Treasury.

1. "Testing by Polariscope" Defined.

The expression "testing * * * degrees by the polariscope," occurring in paragraph 209 of the present tariff act of 1897, is construed to mean the percentage of pure sucrose contained in imported sugar as actually ascertained by polariscopic estimation, and has no reference to the commercial meaning attached to the phrase as recognized in trade between the sellers and buyers of sugar prior to the adoption of said act.

2. Treasury Regulations Valid and Reasonable.

The regulations of the Secretary of the Treasury promulgated under the authority conferred on him by Congress, and designed to carry into effect the provisions of said paragraph, are reasonable and valid, and free from constitutional objections.

3. Constitutional Question—How Raised in Revenue Cases.

Direct appeals from the circuit court of the United States to the Supreme Court, under Section 5 of the act of 1891 (26 Stat., 826), can not be entertained unless the construction or application of some provision of the constitution of the United States is *bona fide* involved, so as to raise a real and substantial dispute or controversy concerning the construction of the constitution upon which the matter in question depends.

United States General Appraisers, New York, December 18, 1908.

In the matter of protests 147213, etc., of American Sugar Refining Company against the assessment of duty by the collector of customs at the port of New York.

Before Board 3 (Waite, Somerville, and Hay, General Appraisers).

Somerville, *General Appraiser:* The importations covered by the protests contained in the schedule consists of sugar which was assessed for duty by the collector under paragraph 209 of the tariff act of July 24, 1897, according to the polariscopic test prescribed by the regulations of the Secretary of the Treasury in order to ascertain the percentage of pure sucrose. These regulations are assailed by the importers variously on the ground that they are unreasonable and invalid, and alleging in some cases that they are unconstitutional. It is further objected in many cases that the phrase used in said paragraph 209, "testing by the polariscope," must be construed to mean the usual commercial polariscopic test as recognized and accepted in the trade between buyers and sellers of sugar at and prior to the adoption of the tariff act of 1897.

Similar questions were under consideration and were decided by this Board as far back as March, 1899, in the case of Bartram Brothers, G. A. 4386 (T. D. 20850), where the protests were overruled and the legality and reasonableness of the regulations were fully sustained. On appeal being taken from that decision to the circuit court, that court reversed the judgment of the Board, holding that the term "testing by the polariscope" had a well-settled commercial meaning prior to 1897, and must be interpreted in accordance therewith. Bartram Brothers *v.* United States (123 Fed. Rep., 327). On further appeal being taken to the circuit court of appeals, that court reversed the circuit court and fully sustained the decision of the Board (131 Fed. Rep., 833; 65 C. C. A., 557; T. D. 25395). In October, 1904, a petition for a writ of certiorari was presented to the Supreme Court in that and other similar cases and was denied (195 U. S., 635; T. D. 25901).

A renewal of all this litigation has taken place recently, where similar questions were again brought under review directly by the Supreme Court of the United States in the case of the American Sugar Refining Company *v.* United States (29 Sup. Ct. Rep. ; T. D. 29411). These appeals were dismissed by the Supreme Court for want of jurisdiction; and the following observations were made by Chief Justice Fuller in delivering the opinion of the court:

By Section 5 of the act of 1891 (26 Stat., 826), the judgments or decrees of the circuit courts of appeals are made final in all cases arising under the revenue law, and can only be carried to the Supreme Court by certificate, or on a certiorari. In the aforementioned cases there was no certificate for instruction on any question or proposition of law, and the application for certiorari was denied. The present direct appeal to this court is a mere attempt to obtain a reconsideration of questions arising under the revenue laws and already determined by the circuit court of appeals in due course. Such direct appeals, under Section 5 of the act of 1891, can not be entertained unless the construction or application of the Constitution of the United States is involved.

This is conceded, and counsel for appellant attempt to sustain the jurisdiction on the ground that the regulations assumed to add something to the dutiable standard prescribed by the tariff act, and that in doing so the Secretary exercised legislative power confided by the Constitution solely to Congress. But this does not constitute a real and substantial dispute or controversy, concerning the construction or application of the Constitution, upon which the result depends.

The admitted duty of the Secretary of the Treasury was to construe as best he could the paragraph relating to collection of duty upon sugars and to promulgate regulations for carrying it into effect (Rev. Stat., Sec. 251). This and this alone he did. The only real substantial point involved is whether or not he misconstrued the statute, and that gives this court no jurisdiction upon direct appeal. Sloan *v.* United States (193 U. S., 614, 620) and cases cited; United States *ex rel.*, etc., *v.* Taft, Secretary (203 U. S., 461).

Undoubtedly, Congress, without violating any constitutional provision, could have in terms directed exactly what was prescribed by the Treasury regulations; and prior decisions have held that the statute was properly construed by the secretary.

We concur with counsel for the government, that if the construction or application of the Constitution of the United States, within the meaning of Section 5, act of 1891, is involved in every case where one claims that according to his interpretation of a statute excessive duty or tax has been demanded by executive officers, the provisions of that act making decisions of the cicuit court of appeals in revenue cases final are of very limited value, and this court must entertain direct appeals from the circuit courts in most tariff and tax controversies, which we regard as out of the question.

The contentions made in these cases are the same as those made in the decision above cited. Following the views of the Supreme Court, as expressed in said decision, we overrule the protests on all grounds and affirm the decision of the collector in each instance.

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EDITORIALS.

EDUCATION.

There have been a large number of papers published within the past year which dealt with the preparation of engineers in general, or of chemists and chemical engineers in particular. Most of them were written by practical engineers. If the teachers of the land have read them all, they are still justified in following their own concepts to a considerable degree, because of the disparity on the one side and impracticability on the other. If the teachers have read but part of them and have been deeply impressed, they may be changing good plans for poorer ones. They may be making the future graduate of their courses still more of a hand-book of ready data and of evanescent processes, of quick conclusions and of decapitated originality. They may be turning out a machine to fit the present requirements of a certain kind of mill, which mill will pay a royalty of sixty dollars a month for the use of the machine, but is this the best attainable? Should not such requirements be considered merely as a fortunate demand for by-products? Are not the "seconds" of the chemist-plant good enough for the mill which wants a cheap machine? The broken saggers of a porcelain factory might be a useful by-product, but should we forget the making of the porcelain?

In chemical industries and engineering, the one thing most needful is character, which means integrity, individuality, energy, push, etc. These must be greater than the average to warrant greater than average success. The memory of the stored facts, the familiarity with the prices and names of common chemicals, the details of their manufacture, etc., need be only an average-grade-accessory. If a man cannot think independently, cannot talk or write decently, cannot listen internally, and finally does not do so frequently and better than the average, then the retention of stored knowledge will be a useless task to him.

It may be maintained that such assets as character, interest, judgment, etc., cannot be poured through a funnel, that they cannot be driven in with a hammer, that they are hereditary in the man or absent forever, but is it true? Are not these desiderata largely the result of intimate contact with such personal qualities as distinct from physical contact with other things? They are not openly demanded of the teacher by the student as he demands chemical knowledge, nor are they likely to be demanded as long as every man feels that he does not need them. But may they be acquired? In practice it is the difference in these traits which is of greater influence than accumulated knowledge, though the latter be ever so necessary. A well-trained engineer in any science will very quickly look and act and become like a well trained chemist if he finds himself called upon to go deeply into chemistry. A poorly trained chemist may have trouble keeping up with the office boy on routine steel analysis if he lets himself latibulize. The deciding difference between

the two is in the personality or character, and not in the stock of knowledge. It seems as though the automatic power of centering and maintaining interest in things was one of the most desired traits to impart to a very young chemist.

W. R. WHITNEY.

THE NEXT STEP IN PUBLICATION FOR THE AMERICAN CHEMICAL SOCIETY.

SEVERAL years ago Professor A. A. Noyes proposed a classification of the articles in the *Journal of the American Chemical Society* with a separate paging for each class. A little more than two years ago the writer presented to the Council of the Society a scheme for the publication of a set of separate journals representing the more important subdivisions of chemistry. The plan proposed was imperfect in some of its details and it involved a coördination of conflicting interests which is probably too Utopian for complete realization. The American Chemical Society has, however, accepted the most vital part of the proposal and has established a separate journal devoted to the interests of industrial and engineering chemistry. Every one will, I am sure, agree that the development of publication has been so rapid recently that we should wait till we can see more clearly the effect of present policies before taking another step forward. It is, however, wise for us to begin to consider the direction which future development should take.

The purposes which have led to the establishment of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY are: First, to care better for the interests of a class of chemists and manufacturers who form a very large group of our membership. Second, to furnish a more suitable medium for the publication of articles in this field in the hope that we may bring a large portion of the best industrial articles together in a single journal where they will be easily accessible to the chemists of the country. Third, to gain new members with the support which they will give. A fourth reason which might apply in other cases would be the desire to combine the articles from some fields of chemistry which is represented in the *Journal of the American Chemical Society* with those published in some existing journal, with the hope of securing for this journal the publication of practically all American work in the field.

All of the reasons given lead many physical chemists in America to desire the publication by the American Chemical Society of a journal of physical chemistry. The difficulty of separating general and physical from inorganic articles, as indicated by German experience, makes it seem desirable to combine the three classes of articles in one journal. Such a journal, if established, would take about two-thirds of the articles which will probably be published in the *Journal of the American Chemical Society* during the present year. Evidently what would be left could no longer be called, appropriately, the *Journal of the American Chemical Society*, and the establishment or adoption by the society of a journal of physical chemistry means also the establishment or adoption of a journal of organic and biological chemistry. This has not, perhaps, been sufficiently considered by the physical chemists.

If we assume that the publication of a journal of physical and inorganic chemistry is desirable, the next questions are those of practical detail. In the first place it is to be hoped that some arrangement can be made, satisfactory to the Editor of the *Journal of Physical Chemistry*, by which the articles published ln the *Journal of the American Chemical Society* can be united with those published in the former.

The financial side of the question is best considered in connection with the different plans which may be proposed:

(1) The journal might be published on a subscription basis. It is extremely doubtful if sufficient financial support could be secured in this way, but, even if it could it would mean that we should take away from one class of members of the American Chemical Society those articles in which they are especially interested, compelling them to do without or pay extra for them. It would, in effect, raise the dues for those interested in physical chemistry. I am sure this is not desirable.

If two journals were published in place of the *Journal of the American Chemical Society*, with an increase of 800 pages of material, and both journals were to go to all our members the additional cost of printing would be about \$2500. If we add \$700 for the salary and expenses of the editor, we have \$3200 a year as the sum needed for the establishment of this journal. This expenditure might be met by one of the following plans:

(2) On payment of the present dues of \$10 members might be permitted to select any three of the four journals which we would then publish.

Any one wishing all four would pay $3 additional. If we assume that 500 would do this (a liberal estimate) this would give $1500, while about $2800 would be saved by the decrease of 3500 copies in the total circulation of the three journals. Such a plan would, in effect, add $3 to the dues of all who wished, as now, to have access to original papers in all fields and would deprive all the rest of the papers in some one field. The increase would be especially felt by students and young men just beginning their professional career. The injury which would result from giving to the majority of our members a one-sided literature appears to me very serious. We ought not to think chiefly of the members of the council of the society and of chemists of similar character and position but rather of members with limited means and of the many who are isolated so that the journals published by the society are the only ones they can see. The decreased circulation would also make the journals less attractive as a means of publication and might also interfere seriously with advertisements.

(3) An increase of $1 in the dues would somewhat more than meet the increased expense. It seems to be generally agreed that such a plan is wholly inadvisable and that the dues must not be increased again for any purpose.

(4) Add 640 new members. Even with the four journals it would cost only about $5 to print an extra copy of each, pay the postage, and pay the additional expenses for the secretary, local sections, etc. Hence each new member adds $5 to the funds available for publication.

(5) Secure an endowment for publication. Every one will admit, I think, that the maintenance of our publications is of very great importance for the future of chemistry in America and it does not seem too much to hope that some of the leaders of industries which have profited so largely by our science may yet contribute liberally to their support. What has been accomplished during the past two years is certainly a sufficient basis for an earnest appeal.

It seems to be clear from what has been said that we ought to wait for the publication of a journal of physical chemistry till it is possible, financially, to do this and send the journal to all of our members. For the first time in the history of chemistry the American Chemical Society has succeeded in uniting all classes of chemists in a large organization which cares adequately for the interests of both pure and applied science. Those of us who attend the general meetings of the society see very clearly the advantages which come from the association and acquaintance of chemists with radically different habits of work and points of view. But we must remember that, after all, these meetings reach only a small fraction of our membership, while the journals now go to all of our members. We have recently provided, by the establishment of this Journal, a more suitable form of publication for articles in industrial and engineering chemistry. I am sure that industrial chemists would be the last to say that we ought not to continue to provide, as in the past, for the suitable publication of researches which have been undertaken without reference to any industrial application.

W. A. Noyes.

SAMPLING.

Mr. Bailey has done a service to analytical chemistry by his careful physical and mathematical investigation of sampling, the results of which are published in this number. While the work concerns itself with the sampling of coal, the results are of wide application. In the past, and at the present time, in thousands of cases the analysis has to bear the criticism which should fall upon improper sampling. The analyst, who is not his own sampler, can analyze only the sample which is delivered to him. Almost any analyst can relate how samples representing carload lots of coal were delivered to him in pint milk bottles and lubricating greases in candy sacks. Members of the engineering profession are not altogether blameless in encouraging faulty sampling, and occasionally the chemist himself is deserving of censure in this regard. The simple truth that a correct analysis is dependent upon a correct sample, would appear to be sufficiently axiomatic to require no demonstration.

W. D. Richardson.

ORIGINAL PAPERS.

THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.[1]

By L. H. Baekeland, Sc.D.

Received February 8, 1909.

Since many years it is known that formaldehyde may react upon phenolic bodies. That this re-

[1] Read before the N. Y. Section of the American Chemical Society on February 5, 1909

action is not so very simple is shown by the fact, that according to conditions of operating or to modified quantities of reacting materials, very different results may be obtained; so that bodies very unlike in chemical and physical properties may be produced by starting from the same raw materials. Some of these so-called condensation products are soluble in water, other ones are crystalline, while some others are amorphous and resinlike. Then again, among the latter resinous products some are easily fusible and soluble in alcohol or similar solvents while other ones are totally insoluble in all solvents and infusible. This paper will deal with a product of the latter class.

The complexity of my subject compels me to make a brief historical outline which will allow us to form a clearer idea of the scope of my work and differentiate it from prior or contemporary attempts in subjects somewhat similar.

That phenols and aldehydes react upon each other was shown as far back as 1872 by Ad. Bayer and others.[1]

The substances obtained by these investigators were merely of theoretical interests and no attempt was made to utilize them commercially; furthermore their method of preparation was too expensive and too uncertain and the properties of some of their resinous products were too undecided to suggest the possibility of utilizing them for technical purposes.

Until 1891 attempts at synthesis with formaldehyde were generally limited to the use of its chemical representatives, either methylal, methylen acetate, or methylen-haloid-compounds.

With the advent of cheap commercial formaldehyde, Kleeberg[2] took up again this subject using formaldehyde solution in conjunction with phenol and in presence of strong HCl. Under spontaneous heating he obtained a sticky paste which soon becomes a hard irregular mass. The latter is infusible and insoluble in all solvents and resists most chemical agents; boiling with alkalies, acids or solvents will merely extract small amounts of apparent impurities.

As Kleeberg could not crystallize this mass, nor purify it to constant composition, nor in fact do anything with it after it was once produced, he described his product in a few lines, dismissed the subject and made himself happy with the study of nicely crystalline substances as are obtained by the action of formaldehyde and polyphenols, gallic acid, etc.

The mass obtained after Kleeberg's method, is a hard and irregular porous substance containing free acid which can only be removed with difficulty after grinding and boiling with water or alkaline solutions. The porosity of the mass is due, as we shall see later, to the evolution of gaseous products during the process of heating.

In 1899 Smith,[1] realizing probably that Kleeberg's method does not lend itself to molding homogeneous articles, tried to moderate the violent reaction by using a solvent like methyl-alcohol or amyl-alcohol in which he dissolves the reacting bodies, as well as the condensing agent, muriatic acid. Even then the reaction is too violent if formaldehyde be used, so he does not use formaldehyde, but instead he takes expensive acetaldehyde and paraldehyde, or expensive polymers of formaldehyde. After the reaction, he slowly evaporates the mixtures and drives off the solvent at 100° C. He thus obtains, by and by, a hardened mass in sheets or slabs which can be sawed, cut or polished. In his German patent specification[2] he insists on the fact that in his process the methyl- or amyl-alcohol not only act as solvents but participate in the reaction and he states that this is clearly shown by the color of the final product, which is dependent on the nature of the solvent he employs. He mentions that his drying requires from 12–30 hours; my own experience is that it takes several days to expel enough of the solvent; and even after several months, there is still a very decided smell of slowly liberated solvent. During the act of drying I observed in every instance warping and irregular shrinking of the mass which thereby becomes deformed and makes this method unfit for accurate molding.

In 1902 Luft,[3] tried to overcome these difficulties in a somewhat similar way. Like Kleeberg he uses a mixture of formaldehyde, phenol and an acid; but recognizing the imperfections of the product and desiring to make of it a plastic that can be molded, he mixes the mass before hardening, with suitable solvents such as glycerine, alcohol or camphor. He virtually does the same thing as Smith with the difference, however, that he adds his solvents *after* the main reaction is partially over and uses his acid condensing agent in aqueous solution. His aim, as clearly expressed in his

[1] *Ber.* 5, 1095; **19**, 3004 and 3009, **25**, 3477, **27**, 2411.
[2] Annalen, **263**, 283 (1891).

[1] Engl. Pat., Arthur Smith, 16247, August 9, 1899.
[2] D. R. P. A. Smith, 112685, October 10, 1899.
[3] D. R. P. Adolf Luft, 140552, April 29, 1902; U. S. P. 735278

patent specifications, is to obtain a mass which remains "transparent and more or less plastic." After pouring his mixture in a suitable mold he dries at a temperature of about 50° C. He too insists on the advantages of using solvents and in his German patent (page 1, line 44) he states that from 2 to 10 per cent. glycerine must remain in the mass; moreover he arranges matters so as to retain in his mixture all the expensive camphor. The whole process of Luft looks clearly like an attempt to make a plastic similar to celluloid and to prepare it and to use it as the latter. The similarity becomes greater by the use of camphor and the same solvents as in the celluloid process.

I have prepared Luft's product; it is relatively brittle, very much less tough and flexible than celluloid; it does not melt if heated although it softens decidedly; acetone swells it and suitable solvents can extract free camphor and glycerine from it.

And now we come to an attempt of another kind, namely the formation of soluble synthetic resins, better known as shellac substitutes.

Blumer[1] boils a mixture of formaldehyde, phenols and an oxyacid, preferably tartaric acid and obtains a fusible, alcohol-soluble, resinous material, which he proposes as a shellac substitute. This substance is soluble in caustic soda lye; it can be melted repeatedly, and behaves like any soluble fusible natural resin. Blumer in his original English patent application puts great stress on the use of an oxyacid and seems to think that the latter participates prominently in the reaction; he uses it in the proportion of one molecule of acid for two molecules of phenol and two molecules of formaldehyde.

Nathaniel Thurlow, working in my laboratory on the same subject, has conclusively shown several years ago that the identical material can be obtained by the use of minute amounts of inorganic acids; he has shown furthermore that equimolecular proportions are not necessary; in fact they are wrong and harmful if the reaction be carried on in such a way that no formaldehyde be lost; he showed also that in order to obtain a fusible soluble resin, an excess of phenol over equimolecular proportions must be used, unless some formaldehyde be lost in the reaction.

So as to avoid confusion, I ought to mention here that Blumer and Thurlow's resin is relatively very brittle, more so than shellac and that no amount of heating alone changes it into an insoluble, infusible product.

As to the real chemical constitution of this interesting product which I have tried to establish by indirect synthesis, I shall read a paper on this subject at one of the next meetings of this society.

About a year later, Fayolle[1] tries to make gutta-percha substitutes by modifying Luft's method: he adds large amounts of glycerine to the sulphuric acid used as condensing agent, and obtains a mass that remains plastic and can be softened and kneaded whenever heat is applied. On trial, this method gave me a brittle unsatisfactory substance of which it is difficult, if not impossible, to wash away the free acid without removing at the same time much of the glycerine. In this relation, Luft's way of adding the glycerine after eliminating the acid, seems more logical.[2]

Later,[3] the same inventor modified his method by adding a considerable amount of pitch ("brai") and oil thus trying to make another gutta-percha substitute which also softens when heated and remains plastic.

In 1905 Story[4] modifies all above methods in the following way: He discontinues the use of condensing agents and of added solvents; but he takes a decided excess of phenol, namely 3 parts of 40 per cent. formaldehyde and 5 parts of 95 per cent. cresol or carbolic acid; by this fact the latter is present in excess of equimolecular proportions. He boils this mixture for 8–10 hours, then concentrates in an open vessel which drives off water and some formaldehyde, and which increases still more the excess of phenol; after the mixture has become viscous he pours it into suitable molds, cools down and afterwards hardens by slow *drying below 100° C.*, or as stated in his patent, at about 80° C. His product is infusible and insoluble. But this method has some very serious drawbacks which I shall describe summarily and which Story himself recognized later.[5]

His process is necessarily slow. Leaving out of consideration his long preliminary boiling, the hardening process at temperatures *below 100° C.* is really a *drying* process where the excess of phenol that provisionally has acted as a solvent is slowly expelled. This assertion I have been able to verify beyond doubt by my direct experiments

[1] Engl. Pat., Louis Blumer, June 5, 1902, No. 12880.

[1] French Pat., E. H. Fayolle, 335584, September 26, 1903.

[2] See also addition patents to original French Pat. add. Pat. 2414, February 8, 1904 and 2485, February 18, 1904. Fayolle.

[3] French Pat., E. H. Fayolle, 341013, March 7, 1904.

[4] Engl. Pat., Henry Story, 8875, 1905.

[5] See his addition Patent, Belgium 210965, September 30, 1908.

where hardening was conducted in closed vessels at below 100° C. and where I succeeded in collecting phenol with the eliminated water. The evaporation or drying process may proceed acceptably fast for thin layers, or thin plates, but for masses of a somewhat larger volume, it requires weeks and months; even then the maximum possible hardness or strength is not reached at such low temperatures. All this not merely involves much loss of time, but the long use of expensive molds, a very considerable item in manufacturing methods; furthermore, during the act of drying, the evaporation occurs quickest from the exposed surface, thus causing irregular contraction and intense stresses, the final result being misshapen molded objects, rents or cracks.

Story states that if pure phenol be used the reaction proceeds very slowly; I should add that in that case the reaction does not take place, except very imperfectly, even after several days of continuous boiling. Even then in some of my own experiments made with pure commercial crystallized phenol and with commercial 40 per cent. formaldehyde, I obtained products not of the insoluble type, but similar to the soluble fusible products of Blumer and Thurlow.

Taken in a broad sense, Story's process is very similar to Luft's with this difference however, that he foregoes the use of an acid condensing agent and instead of using a solvent like alcohol, glycerine or camphor, he uses a better and cheaper one, namely an excess of phenol. In further similarity with Luft and Smith's his method is, as he expresses himself in his patent text, a *drying* process.

Like Smith and Luft he is very careful to specify temperatures *not* exceeding 100° C. for drying off his solvent.

Shortly after Story filed his patent, DeLaire[1] obtained a French patent for making soluble and fusible resins either by condensing phenols and formaldehyde in presence of acids, in about the same way as Blumer or Thurlow and then melting this product; or by dissolving phenol in caustic alkalies *used in molecular proportions*, then precipitating the aqueous solution with an acid and afterwards resinifying the reprecipitated product by heating it until it melts. I should remind you that the French patent laws allow patents without any examination whatever as to novelty. And I should state also that DeLaire simply uses here

[1] French Pat., DeLaire 361539, June 8, 1905.

the old and well-known processes of Lederer[1] and Manasse[2] which consists in making a phenol-alcohol by the action of formaldehyde on an aqueous solution of a phenolate and subsequent treatment with an acid.

It is a well-known fact that these phenol-alcohols, for instance saligenin, if heated alone or with an acid, will give partial anhydrides such as saliretin and homosaliretin,[3] $C_{14}H_{14}O_3$ or $C_6H_4(OH)CH_2OC_6H_4CH_2OH$,[4] fusible and soluble in alcohol, or caustic soda, and precipitable from the latter by the addition of chloride of sodium.

Trisaligenosaligenin, $C_{28}H_{26}O_5$ or $4C_7H_8O_2-3H_2O$,[5] and heptasaligenosaligenin, $C_{56}H_{50}O_9$ or $8C_7H_8O_2—7H_2O$,[6] are both higher anhydrides of similar resinous character, the first one obtained by the action of sulphuric acid on saligenin, the latter by the action of acetic anhydride.

The direct homolog of saliretin, which is methylsaliretin or homosaliretin, has properties similar to saliretin, melts at 200° or 205° C. and is less soluble.[7]

No wonder then if the English[8] and the German patents[9] of DeLaire vary considerably in text and claims from the French patent; the claims are reduced merely to a method consisting in resinifying phenol-alcohols by heating them under reduced pressure or vacuum. The resins of DeLaire are fusible, soluble products, having all the general properties of saliretin and homosaliretin.

In order to complete my enumeration of methods where alkalies are used, I ought to mention two processes which aim at products very different from those which we have in view. Speyer[10] produces an antiseptic which easily gives off CH_2O. For this purpose he uses naphthol or polyphenols like resorcin or pyrogallol and adds an excess of ammonia and of formaldehyde. This gives him an insoluble powder which easily liberates CH_2O and NH_3. It is a well-known fact that ammonia reacts on formaldehyde and produces hexamethylentetra-

[1] *Journal Praktische Chemie* [2], vol. 50, page 224.

[2] *Ber.*, 1894, 2409–2411, D. R. P. Bayer, 85588, U. S. P., Manasse, 526786, 1894.

[3] Beilstein, *Organ. Chemie*, Vol. 2, 1896, page 1109.

[4] R. Piria, *Ann. Chem.*, **48,** 75, **56,** 37, **81,** 245; **96,** 357. Moitessier, Jahresbericht, 1886, page 676.

[5] K. Kraut, *Ann. Chem.*, **156,** 123, Gerhardt, *Ann. Chim. Phys.* [3], 7, page 215.

[6] F. Beilstein and F. Seelheim, *Ann. Chem.*, 117, page 83.

[7] C. Schotten, *Berichte*, 1878, page 784.

[8] Engl. Pat., DeLaire, 15517, 1905.

[9] D. R. P., DeLaire, 189262, July 19, 1905.

[10] D. R. P., Arthur Speyer, 99570, November 2, 1897.

min, $C_6H_{12}N_4$,[1] which easily acts upon acids and forms again CH_2O, NH_3 and methylamin.[2]

Two recent patents relate directly to the manufacture of soluble fusible resins. One of Farbenfabriken Fried. Bayer & Co.[3] uses orthocresol so as to obtain an odorless shellac substitute.

The other issued to Grognot[4] also for a shellac substitute, adds glycerine first, then after the reaction is over distils the solvent off.

After I had filed my own patent claims in the U. S. which gave me International Convention privileges, Helm[5] described, after me, amines or ammonium salts as condensing agents for the manufacture of synthetic resins with phenols and formaldehyde. He does not clearly indicate the chemical or physical properties of his resins. He furthermore makes the rather ambiguous statement that ammonium nitrate can be used as well as aniline. I have shown (see below) that in the case of ammonium nitrate the end-product may be a fusible soluble resin, while in the case where aniline is used I obtain finally an insoluble infusible resin.

It is true that Helm uses large amounts of aniline and nitrate of ammonium; his indicated proportions are very close to molecular proportions and this undoubtedly has, as I will show later, a great influence on the nature of the resulting products.

Knoll,[6] who also applied for patents after the filing date of my U. S. patents, uses sodium sulphite or *neutral*, or *acid* or *alkaline* salts as condensing agents; disregarding again the fact established by me, that according to whether an acid, a base, an acid salt, or an alkaline salt be used, the resinous products may be totally different.

This will close my review of the work done by others and I shall begin the description of my own work by outlining certain facts, most of which seem to be unknown to others, or if they were known their importance seems to have escaped attention. Of these facts I have made the foundation of my technical processes.

As stated before, the condensation of phenols with formaldehyde can be made to give, according to conditions and proportions, two entirely different classes of resinous products. *The first class* includes the products of the type of Blumer, DeLaire, Thurlow, etc. These products are soluble in alcohol acetone or similar solvents, and in alkaline hydroxides. Heating, simply melts them and they resolidify after cooling. Melting and cooling can be repeated indefinitely but further heating will not transform them into products of the second class. They are generally called "*shellac substitutes*," because they have some of the general physical properties of shellac.

The second class includes the products of Kleeberg, Smith, Luft, Story, Knoll as well as my own product, in so far only as their general properties are concerned; but each one of them may be characterized by very distinct specific properties which have a considerable bearing on any technical applications. Broadly speaking, this second class can be described as infusible resinous substances, derived from phenols with aldehydes; some of them are more or less attacked by acetone, by caustic alkalies or undergo softening by application of heat. *At least one of them* is unattacked by acetone and does not soften even if heated at relatively high temperatures. None of them can be re-transformed into products of the first class even if heated with phenol.

These insoluble infusible substances can be produced directly in one operation by the action of formaldehyde on phenols under suitable conditions, for instance the process of Kleeberg (see above). Or they may be produced in two phases (see Luft and Story above), the first phase consisting of an incomplete reaction giving a viscous product that is soluble in alcohols, glycerine, camphor or phenol, and which on further heating or after driving off the solvent may gradually change into an infusible product.

In order to be able to stop at the first phase, the condensing agents may either be omitted (see Story above) or they may be used moderately (see Luft above) or they may be diluted with suitable solvents, for instance methyl- and amyl-alcohol (see Smith above) or with glycerine (see Fayolle above).

In all these processes there is a further treatment by which the solvent is driven off during a *drying* process. For example, in the process of Smith or Luft, alcohol or glycerine is thus expelled partially; and in Story's process the excess of phenol is driven off in the same way by slow

[1] Wohl, *Ber.*, **19**, 1892; Tollens, *Ber.*, **17**, 653.

[2] See also Moschatos and Tollens, *Ann. der Chemie.*, **272**, 280.

[3] D. R. P., Farbenfabriken vorm. Friedr., Bayer & Co., 201,261, April 16, 1907.

[4] L. Grognot, U. S. P. 391436, 1908.

[5] Engl. Pat., Louis Helm, 25216, November 13, 1907.

[6] Eng. Pat., Knoll & Co., 28009, December 19, 1907; Swiss Pat., Ditto, 40994, December 7, 1907.

drying under 100° C. In all these drying processes, some of the solvent is left, either purposely, so as to insure flexibility or plasticity, or it is left involuntarily, because at temperatures of 100° C. or below it is impossible to expel the totality of these solvents, part of which are stubbornly retained by the mass.

If I except the processes of Blumer, Thurlow or DeLaire, and generally those which have in view fusible and soluble resins, in all above-mentioned patent specifications temperatures *of 100° C. or much below* are insisted upon.

And yet I have convinced myself by often repeated experiments that temperatures *above 100° C.* and *considerably above 100° C.* are best suited or indispensable for the complete and rapid transformation into a final insoluble, infusible product of exceptionally desirable qualities. If this be so why have my predecessors not used temperatures above 100° C.?

Why do some of them recommend temperatures as low as 80° C. (Story) and even 50° C. (Luft)? Why do they prefer to make this final hardening a long and slow operation which does not give the best, the hardest, the most resisting product? (See confirmation of my statement by Story in Belgian addition patent 210965, September 30, 1908.)

For the simple reason that if their initial mass be heated at too high a temperature it gives off gaseous products, mainly composed of formaldehyde; this produces bubbles in the mass, makes it spongy, porous, and unfit for commercial use.

More direct experiments have proved to me that during the first stages of the process, we have to deal with a phenomenon that has all the characteristics of chemical dissociation with liberation of CH_2O.

If the initial mass be heated at temperatures above 100° C. the tension of this gas becomes very pronounced. At 100° C. the tension may become as high as 1 kilogram per square centimeter (above atmospheric pressure), but this tension subsides as soon as the final product is formed.

I shall explain later how I have utilized this knowledge to good advantage, and how I counteract this dissociation simply by exercising a compensating external pressure.

In the historical part of my paper, reference has repeatedly been made to the use of condensing agents. We have seen how Kleeberg, Smith, Luft, Fayolle, Blumer and Thurlow use acid condensing agents. Others like Speyer, Hentsche, Lederer, Manasse, DeLaire, use alkalies, but every time in relatively large proportions: practically one molecule or over; but the products thus obtained are of a nature very different from the substance I am about to describe.

Story, on the other hand, adds no condensing agents whatever. True, he is able, with commercial impure carbolic acid, to obtain a reaction after about 8–10 hours' boiling, and this heating process has then to be supplemented by much longer drying. But if his process be carried out with pure or crystallized phenol, it takes many days of continuous boiling before a reaction sets in; even then the product obtained is of a dubious character hovering between a resin of class one (fusible and soluble) and a resin of class two (infusible and insoluble). It is more likely to be a fusible and soluble resin if for some reason or another the process has been carried out with an excess of phenol or if, some way or another, too much CH_2O has escaped in the after concentration. For instance by following his description and boiling for 5 days in a return condenser a mixture of 50 gr. pure crystalline phenol and 30 gr. 40 per cent. commercial formaldehyde, then concentrating in an open dish, I obtained the fusible soluble resin of Blumer or Thurlow which on further heating remains fusible and does not change into the insoluble infusible product as described by Story. I obtain the same result if the boiling be carried on in presence of a small amount of any acid, any acid salt, or any salt which on hydrolyzing may split, so as to give a preponderant acid reaction. This effect is shown by salts of mineral acids and heavy metals; it is shown even with ammonium chloride, and on acting upon formaldehyde liberates free hydrochloric acid.[1]

On the other hand, if I use an alkaline salt or a salt, which on hydrolyzing splits into a weak acid and a strong base, as for instance sodium acetate, I obtain under the same circumstances a resin of the insoluble, infusible variety even if to some extent, a slight excess of phenol has been used, showing conclusively that within certain limits the amount of phenol does not change the general character of the reaction. All what may happen in that case is that the final product is rendered impure by some excess of phenol which can be

[1] See Cambier, Brochet, *Compt. rend.*, **120**, 557.

driven off afterwards by a drying process similar to that of Story.

I have obtained similar results with many other alkaline salts as for instance ammonium carbonate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, borax, potassium cyanide, sodium silicate, soap, etc.

In the same way I have used sodium sulphite, which on acting on CH_2O liberates sodium hydroxide according to following reaction:

$$CH_2O + SO_3Na_2 + H_2O = CH_2(OH)SO_3Na + NaOH.$$

I might say that a similar effect is obtained from all substances which can act directly or indirectly as bases.

In other terms: *the quality as well as the quantity* of condensing agent has an enormous influence on the nature of the final products.

For the manufacture of insoluble, infusible, condensation products of formaldehyde and phenol, bases used in moderate amounts have very decided advantages. They accelerate the reaction without degenerating same into a violent and irregular process. The relatively small amount of base which may remain present in the finished product, either in combined or uncombined form, does not involve the same objectionable features for its technical uses as the presence of free acid.

Furthermore, for some reason or another acid condensing agents seem to favor the formation of soluble and fusible resins, while for some other reason, bases seem to favor the formation of insoluble, infusible resins.

Moreover, by the use of small amounts of bases, I have succeeded in preparing a *solid* initial condensation product, the properties of which simplify enormously all molding operations as we shall see later.

I have tried all organic or inorganic bases which I could obtain readily. I have tried the hydroxides and carbonates of the alkali metals, the hydrates of alkaline earths, ammonia and its alkaline salts, hydroxylamin, organic amines, pyridine, carbamide and other amides of weak acids; and the effect, with slight variations, is always about the same; it is quite natural, that for reasons of economy or expediency, I should prefer the commercially more available bases.

I wish it distinctly understood that in order to obtain my technical effect I use the bases in relatively small quantities, say less than one-fifth of the amount which would be required to transform the phenol into phenolate.

If larger amounts of base be used, the results are technically much inferior; in fact the process changes gradually into such as give phenol-alcohols or compound condensation products of ammonia or amines with formaldehyde, all products very different from those I desire to make.

I have good reason to believe that in my process the bases only act as catalyzers and intervene only temporarily in the reaction. They seem to be expelled in free condition during the last stage of the process. For instance if I use ammonia, I find this ammonia back in the free state in the final hard condensation product.

A careful study of the condensation process of phenols and formaldehyde, made me discover that this reaction instead of occurring in two stages can be carried out in three distinct phases. This fact is much more important than it appears at first sight. Indeed it has allowed me to prepare a so-called *intermediate condensation product*, the properties of which simplify still further my methods of molding and enlarge very much the scope of useful applications of my process.

The three phases of reaction can be described as follows:

First phase. The formation of a so-called *initial condensation product* which I designate as *A*.

Second phase. The formation of a so-called *intermediate condensation product*, which I designate as *B*.

Third phase. The formation of a *final condensation product*, which I designate as *C*.

As to the properties of each of these condensation products I can define them in a few words:

A, at ordinary temperatures, may be liquid, or viscous, or pasty, or solid. Is soluble in alcohol, acetone, phenol, glycerine and similar solvents; is soluble in NaOH. *Solid A* is very brittle and melts if heated. All varieties of *A* heated long enough under suitable conditions will change first into *B* then finally into *C*.

B is solid at all temperatures. Brittle but slightly harder than solid *A* at ordinary temperatures: insoluble in all solvents but may swell in acetone, phenol or terpineol without entering into complete solution. If heated, does not melt but softens decidedly and becomes elastic and somewhat rubber-like, but on cooling becomes again hard and brittle. Further heating under suitable conditions changes it into *C*. Although *B* is

infusible it can be molded under pressure in a hot mold to a homogeneous, coherent mass, and the latter can be further changed into *C* by the proper application of heat.

C is infusible, insoluble in all solvents; unattacked by acetone, indifferent to ordinary acids, or alkaline solutions; is destroyed by boiling concentrated sulphuric acid, but stands boiling with diluted sulphuric acid; does not soften to any serious extent if heated, stands temperatures of 300° C.; at much higher temperatures begins to be destroyed and chars without entering into fusion. It is a bad conductor of heat and electricity.

The preparation of these condensation products *A* and *B* and their ultimate transformation in *C* for technical purposes constitute the so-called Bakelite process. This can be described easily:

I take about equal amounts of phenol and formaldehyde and I add a small amount of an alkaline condensing agent to it. If necessary I heat. The mixture separates in two layers, a supernatant aqueous solution and a lower liquid which is the initial condensation product. I obtain thus at will, either a thin liquid called *Thin A* or a more viscous mass, *Viscous A* or a *Pasty A*, or even if the reaction be carried far enough, a *Solid A*.

Either one of these four substances are my starting materials and I will show you now how they can be used for my purposes.

If I pour some of this *A* into a receptacle and simply heat it above 100° C., without any precaution, I obtain a porous spongy mass of *C*. But bearing in mind what I said previously about dissociation, I learned to avoid this, simply by opposing an external pressure so as to counteract the tension of dissociation. With this purpose in view, I carry out my heating under suitably raised pressure, and the result is totally different.

This may be accomplished in several ways but is done ordinarily in an apparatus called a Bakelizer. Such an apparatus consists mainly of an interior chamber in which air can be pumped so as to bring its pressure to 50 or better 100 lbs. per square inch. This chamber can be heated externally or internally by means of a steam jacket or steam coils to temperatures as high as 160° C. or considerably higher, so that the heated object during the process of Bakelizing may remain steadily under suitable pressure which will avoid porosity or blistering of the mass.

For instance if I pour liquid *A* into a test tube and if I heat in a Bakelizer at say 160 180° C., the liquid will change rapidly into a solid mass of *C* that will take exactly the shape of its container; under special conditions it may affect the form of a transparent hard stick of Bakelite. It is perfectly insoluble, infusible, and unaffected by almost all chemicals, an excellent insulator for heat and electricity and has a specific gravity of about 1.25.

It is very hard, cannot be scratched with the finger nail; in this respect it is far superior to shellac and even to hard rubber. It misses one great quality of hard rubber and celluloid, it is not so elastic nor flexible. Lack of flexibility is the most serious drawback of Bakelite. As an insulator, and for any purposes where it has to resist heat, friction, dampness, steam or chemicals it is far superior to hard rubber, casein, celluloid, shellac and in fact all plastics. In price also it can splendidly compete with all these.

Instead of pouring liquid *A* into a glass tube or mold I may simply dip an object into it or coat it by means of a brush. If I take a piece of wood, and afterwards put it into a Bakelizer for an hour or so, I am able to provide it rapidly with a hard brilliant coat of Bakelite, superior to any varnish and even better than the most expensive Japanese lacquer. A piece of wood thus treated can be boiled in water for hours without impairing its gloss in the slightest way. I can dip it in alcohol or other solvents, or in chemical solutions and yet not mar the beautiful brilliant finish of its surface. But I can do better, I may prepare an *A*, much more liquid than this one, and which has great penetrating power, and I may soak cheap, porous soft wood in it, until the fibres have absorbed as much liquid as possible, then transfer the impregnated wood to the Bakelizer and let the synthesis take place in and around the fibres of the wood. The result is a very hard wood, as hard as mahogany or ebony of which the tensile- and more specially the crushing strength, has been considerably increased and which can stand dilute acids or water or steam; henceforth it is proof against dry rot. I might go further and spend a full evening on this subject alone and tell you how we are now bringing about some unexpected possibilities in the manufacture of furniture and the wood-working industry in general. But I intend to devote a special evening to this subject and show you then how with cheap soft wood we are able to accomplish results which never have been obtained even with the most expensive hard wood.

In the same way I have succeeded in impregnating cheap ordinary cardboard or pulp board and changing it into a hard resisting polished material that can be carved, turned and brought into many shapes. I might take up much more of your time by simply enumerating to you the applications of this impregnation method, with wood, paper, pulp, asbestos, and other fibrous and cellular materials; how it can be applied for fastening the bristles of shaving brushes, paint brushes, tooth brushes, how it can be used to coat metallic surfaces with a hard resisting protecting material; how it may ultimately supplant tin in canning processes; but I have no doubt that your imagination will easily supply you a list of possible technical uses even if I defer this subject for some other occasion.

As to Bakelite itself, you will readily understand that it makes a substance far superior to amber for pipe stems and similar articles. It is not so flexible as celluloid, but it is more durable, stands heat, does not smell, does not catch fire and at the same time is less expensive.

It makes excellent billiard balls of which the elasticity is very close to that of ivory, in short it can be used for similar purposes like knobs, buttons, knife handles, for which plastics are generally used. But its use for such fancy articles has not much appealed to my efforts as long as there are so many more important applications for engineering purposes.

Bakelite also acts as an excellent binder for all inert filling materials. This makes, that it can be compounded with sawdust, wood pulp, asbestos, coloring materials, in fact with almost anything the use of which is warranted for special purposes. I cannot better illustrate this than by telling you that here you have before you a grindstone made of Bakelite and on the other hand a self-lubricating bearing which has been run dry for nine hours at 1800 rev. per minute without objectionable heating and without injuring the quickly revolving shaft.

If I mix Bakelite with fine sand or slate dust I can make a paste of it which can be applied like a dough to the inside of metallic pipes or containers, or pumps, and after Bakelizing, this gives an acid proof lining very useful in chemical engineering.

Valve seats, which are unaffected by steam, steam-packing that resists steam and chemicals, have been produced in a similar way.

Phonograph records have been made with it, and the fact that Bakelite is harder than rubber, shellac, or kindred substances indicates advantageous possibilities in that direction.

For the electrical industry, Bakelite has already begun to do some useful work. There too its possible applications are numerous. Armatures or fields of dynamos and motors, instead of being varnished with ordinary resinous varnishes, can simply be impregnated with *A*, then put into a Bakelizer and everything transformed into a solid infusible insulating mass; ultimately this may enable us to increase the overload in motors and dynamos by eliminating the possibility of the melting or softening of such insulating varnishes as have been used until now. But the subject of dynamos and motor construction is only at its very modest beginnings and I prefer to mention to you what has been already achieved in the line of molded insulators of which you will find here several very interesting samples.

This brings me to the subject of molding Bakelite.

For all plastics like rubber, celluloid, resins, etc., the molding problem is a very important one. Several substances which otherwise might be very valuable are useless now because they cannot economically be molded. The great success of celluloid has mainly been due to the fact that it can easily be molded. Nitrated cellulose alone, is far superior in chemical qualities to celluloid, but until Hyatts' discovery, it could only be given a shape by an evaporation process and its applications were very limited. The addition of camphor and a small amount of solvent to cellulose nitrate was a master-stroke, because it allowed quick and economic molding.

In the same way white sand or silica would be an ideal substance for a good many purposes, could it be easily compressed or molded into shape and into a homogeneous mass. But it *cannot*; and therefore remains worthless. And that is the main difference between a *plastic* and a *non-plastic*. It so happens that Bakelite in *C* condition does not mold; it does not weld together under pressure even if heated; only with much effort is it possible to shape some kind of an object out of it, but someway or another the particles do not stick well together; in other terms it is not a true plastic. Therefore the molding problem has to be solved in the anterior stages of the process. We have seen how

Smith, Luft, and Story tried to solve a similar problem by the admixture of solvents and subsequent evaporation, but we know now that these very solvents imply most serious drawbacks.

I have already shown you how I am able to mold and harden quickly by pouring liquid *A* into a mold and heating it in a Bakelizer. But even that method is much too slow for most purposes. Furthermore, molds cost money; any rubber or celluloid manufacturer will tell you that the item of molds represents a big portion of the cost of his plant. If an order for 10,000 pieces has to be delivered and it takes an hour for molding, it will require between three and four years to fill this order with one mold and if the mold costs $100 it will require $5000 for molds alone if the order has to be finished within 20 days. For that very reason I have devised my molding methods so as to use the molds only during the very minimum of time. I have succeeded in doing so in several ways. One of the simplest ways is the following:

As stated before, the use of bases permits me to make a variety of *A* that is solid although still fusible. The latter is as brittle as ordinary rosin and can be pulverized and mixed with suitable filling materials. A mixture of the kind is introduced in a mold and put in the hydraulic press, the mold being heated at temperatures preferably about or above 160–200° C. The *A* melts and mixes with the filler, impregnating everything; at the same time it is rapidly transformed into *B*. But I have told you that *B* does not melt, so the molded object can be expelled out of the mold after a very short time and the mold can again be refilled. All the molded articles are now in *B* condition; relatively brittle but infusible. At the end of the day's work or at any other convenient time all the molded articles are put in the Bakelizer and this of course without the use of any molds; in this way they are finally transformed in "*C*" Bakelite of maximum strength and hardness and resisting power.

The process can still be further simplified. Instead of using *A*, we can use *B* and mold it in the hot press where it welds and shapes itself. After a very short time, the *B* begins to transform into *C* and can now be expelled from the mold. If the transformation in *C* is not complete, a short after-treatment in the Bakelizer will finish everything. I have succeeded thus in reducing the molding to less than two minutes for small objects.

The valuable properties of *B* may be used in many other ways; for instance *A* may be poured into a large container and be heated slowly at 70° C. until it sets to a rubber-like mass and shows that it is transformed into *B*. This block of *B* if warm has very much the consistency of printers' roller-composition, but is brittle when cold. The warm flexible mass can now be removed from its container or, divided, cut, or sawed to any desired shape and the so-shaped articles can be simply placed in a Bakelizer; no melting nor deformation can occur, so we need no mold while maximum heat is applied to bring everything in condition *C*.

I could multiply these examples by numerous other modifications of my process but I believe that what I have said will be enough to convince you of its many uses; we are studying now applications of Bakelite in more than forty different industries on some of which I shall report on some future occasion.

The chemical constitution of Bakelite and the nature of the reactions which occur in the Bakelite process are problems which I have endeavored to solve. This subject is not by any means an easy one. Indeed, we have to deal here with a product that cannot be purified by crystallization nor other ordinary methods, which is insoluble, does not melt nor volatilize; in other terms, it is not a product which is amenable to our usual methods of molecular weight determination. Its chemical inertness makes it unfit for studying possible chemical transformations and unless my friends, the physico-chemists, will come to my aid, discover some way for establishing some optical properties or other physical constants, we are very much at a loss to establish the molecular size of my product.

But I have been so fortunate as to be able to obtain some insight into its chemical constitution by a rather round-about way: Indeed, I have succeeded in making Bakelite by indirect synthesis.

As stated previously, oxybenzylalcohol if heated at 150° C., or in presence of acids, gives various partial anhydrides, called saliretin , which may resinify further if heated at higher temperatures. Saliretin products are more or less soluble in alcohol and acetone and in NaOH solution, from which they may be reprecipitated by means of NaCl.

We have already seen that DeLaire in heating phenol alcohols in vacuum obtains soluble resins. But I have heated saligenin in sealed tubes under

pressure at 180° C. for 8 hours, with and without the addition of small amounts of ammonia. In both cases I obtain a substance which is hard when cold, but which softens when heated, but does not melt. It swells in acetone and in NaOH and dissolves partially. This substance is not my intermediate condensation product *B*, because no amount of heating can transform it in *C*.

If, however, I heat oxybenzylalcohol in presence of enough CH_2O or its polymers in a sealed tube at 180° C. for 8 hours, I obtain a substance entirely similar to Bakelite in properties and in chemical composition.

By varying the proportions and repeating the experiment a great number of times I succeeded in establishing that, unless I use at least 1 molecule of CH_2O for 6 molecules of oxybenzylalcohol I do not obtain Bakelite but a product containing saliretin compounds.

The same result occurs by heating 6 molecules of phenol and 7 molecules of CH_2O in presence of a small amount of a base.

If I use somewhat less formaldehyde or if for some reason or another all the formaldehyde does not enter into reaction, I obtain a substance which may still be attacked by acetone, probably because it contains uncombined phenol or saliretins after the reaction is over.

But I have found that all these substances, whether they are obtained by heating 6 molecules of phenol alcohol with at least one molecule of CH_2O, or whether they are obtained by the action of phenol on formaldehyde under heat and pressure in presence of small amount of bases, can be purified and brought to about constant composition as follows:

The substance is pulverized, washed with 5 per cent. KOH solution, with dilute HCl, with alcohol, with acetone and finally dried to constant weight in v_cuo.

The powder so obtained still contains traces of potassium, which I did not succeed in eliminating. The amount of same is very small, about 0.09 per cent. of ash, but it seems to cling tenaciously to the product and makes it somewhat hygroscopic making weighing for analytical purposes very d fficult, and accounts for some variations in the results.

The organic combustion of all these products gave the following results:

1 mole CH_2O, 6 mole saligenin	C = 77.48	77.88
	H = 5.96	5.97
	O = 16.56	16.15
1 mole CH_2O, 4 mole saligenin	C = 76.47	76.35
	H = 5.44	5.40
	O = 18 09	18.25
13 mole CH_2O, 12 mole saligenin	C = 76.59	76.57
	H = 5.97	5.97
	O = 17.44	17.46
1 mole phenol, 1 mole CH_2O and 1 per cent NH_3	C = 77.48	76.61
	H = 5.60	5.80
	O = 16.92	17.59
10 cc. phenol, 10 cc. 40 per cent. formaldehyde and ½ per cent. NH_3	C = 77 92	75.62
	H = 5.71	5.78
	O = 16.37	18.60[1]

If we take into consideration the great difficulties encountered in purifying methods, these results seem to indicate that we have to deal here with a definite organic substance of constant composition, which according to its methods of preparation may exist with impurities mixed in various proportions. These impurities are probably free phenol, or free CH_2O or saliretin products.

From the indirect synthesis of Bakelite by means of oxybenzylalcohol and CH_2O, I am led to consider Bakelite in its simplest form as a polymerized oxybenzyl — methylen - glycol — anhydride which, in case of ordinary phenol, might be represented by the following formula:

$$n(C_{43}H_{38}O_7).$$

The reaction being represented by:

$$n(6C_7H_8O_2 + CH_2(OH)_2) = n(C_{43}H_{38}O_7) + n(7H_2O.)$$

This formula corresponds ac eptably to the analytical results if we take in consideration the difficulties of purification.

	C.	H.	O.
Calculated	= 77.44	5.75	16.81
Found (average)	= 77.68	5.96	16 36

(with product of 6 mole saligenin + 1 mole CH_2O).

I consider Bakelite *C* as a direct polymer of another anhydride which is represented by my intermediate condensation product or Bakelite *B*. Bakelite *B* is a more complete anhydride than Bakelite *A*. As to Bakelite *A*, I am unable to arrive at a constant composition, for the reason that it easily gives off water, changing gradually its composition until heating converts it slowly into *B*, after passing through various mixtures of *A* and *B*.

My supposition has a strong appearance of probability by the following experiment:

If I put a mixture of phenol and formaldehyde in proper proportions and with some small amount of a base in a sealed glass tube and heat just long enough to produce *A* the formerly homogeneous liquid mixture separates into two layers. The initial condensation product *A* forms a lower stratum, and a supernatant layer of liquid indicates the elimination of water. The same thing occurs if

[1] Beginning oxidation during drying.

anhydrous phenol is heated with paraform in presence of a small amount of base.

If this *A*, first properly freed from any physically retained water, be introduced into another sealed tube and heated further, I may succeed, with some precaution as to the duration of heating, in stopping just in time so as to transform everything into *B*, the intermediate condensation product. I then see that a new amount of water is set free which will assemble on top, giving evidence of further dehydration. At the same time we notice that the mass *B* has not contracted in volume to any important extent.

If now this *B*, properly freed from water, be heated in another sealed tube, it will be transformed finally into *C*. But this time we see no further elimination of water. On the other hand there is a decided contraction of volume.

This contraction of volume, together with the remarkable increase in physical and chemical inertness, points out towards the probability that *C* is simply the polymer of *B*.

I am fully supported in this belief by the fact that analysis has shown me that *B* and *C* contain the same percentage of carbon, hydrogen and oxygen.

With homologs of phenol we obtain the direct homologs of these anhydrides; for instance with orthocresol we get the polymer of ortho-methyl-oxybenzyl-methylen-glycol-anhydride.

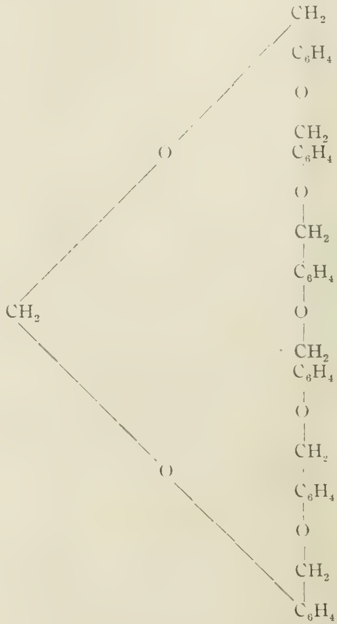
It may be of interest to remind you that many years ago, Oscar Low[1] called our attention to the great importance of formaldehyde as a starting point of synthesis in plant life. By the photochemical action of sunlight on CO_2 in presence of water in chlorophyl, oxygen is liberated and produces CH_2O. This is the beginning of a process of further synthesis building up more complicated bodies.

If we accept these premises then the theory of the Bakelite process is easy to explain:

Stage A.—Formation of a partial anhydride of a phenol alcohol and methylen glycol containing, hydroxyl groups, which can fix NaOH.

Stage B.—Formation of a higher anhydride by further elimination of water. This higher anhydride seems no longer to possess hydroxyl groups, but by addition of NaOH may still form alkaline compounds. This induces me to believe that in some way or another we shall suceed in obtaining alkali compounds of the kind which on being treated with dilute acids will regenerate *A*.

Until we have anything better, I shall propose the formula:



Stage *C*.—Polymerization of the *B* product resulting in greater chemical inertness and disappearance of active corners of the molecule.

I shall also call your attention to the fact that the willow tree produces in its cells, salicin, which is the glucoside of saligenin; this same saligenin or oxybenzyl alcohol in presence of more CH_2O has given me Bakelite.

On the other hand Bertrand,[1] and Vlchirch and Stevan[2] and more recently R. Majima and S. Cho[3] have called our attention to the phenolic nature of resinous substances, specially Japanese lacquer. The latter substance has some analogy with Bakelite and exudes from the *Rhus vernicifera Dc.* which is a plant that is somewhat related to our American "poison ivy."

[1] *Ber.*, **22**, 475 and **23**, 388 and 480.

[1] *Ann. Chim. Phys.* [6], **12**, 115 (1898); *Bull. Soc. Chim.* [3], **11**, 614 and 717 (1894).

[2] Tschirch und Stevan, *Arch. d. Pharm.*, **243**, 504 (1905).

[3] *Ber.*, **15**, November, 1907, page 4390.

So after all, the synthesis accomplished in my laboratory seems to have a decided similarity to some intricate biological processes that take place in the cells of certain plants.

In order not to increase too much the length of this paper, I have merely given you the brief outlines of years of arduous but fascinating work, in which I have been ably helped by Mr. Nathaniel Thurlow and more recently also by Dr. A. H. Gotthelf, who attended to my analytical work.

The opened field is so vast that I look forward with the pleasure of anticipation to many more years of work in the same direction.

I have preferred to forego secrecy about my work relying solely on the strength of my patents as a protection.

It will be a great pleasure to me if in doing so, I may stimulate further interest in this subject among my fellow chemists and if this may lead them to succeed in perfecting my methods or increase still further the number of useful applications of this interesting compound.

(CONTRIBUTION FROM THE ARTHUR D. LITTLE LABORATORY OF ENGINEERING CHEMISTRY.)

ACCURACY IN SAMPLING COAL.[1]

BY E. G. BAILEY

In 1899 the American Chemical Society was presented with a "Report of the Committee on Coal Analysis;" and so far as the chemical analysis is concerned the method recommended by this committee has been very closely followed by the majority of laboratories. In many specifications for the purchase of coal on the analysis and heat unit basis, it is stated that the sample shall be analyzed in accordance with the method adopted by the American Chemical Society, while the greater number of these specifications merely mention the sampling of the coal delivered and do not state definitely how the sample shall be taken and quartered down.

One specification covering the delivery of about 200,000 tons of coal per year states: "Sampling will be done by a representative of the company and contractor may have a representative present. Sample will be taken from each delivery and kept in hermetically sealed jars." Another specification on which almost twice this amount of coal is purchased describes the sampling as follows: "A small quantity of coal will be taken from each weighing hopper just before the hopper is dumped, while the lighter is being unloaded. These quantities will be thrown into a receptacle provided for the purpose, and when the lighter is empty the contents of the receptacle will be thoroughly mixed, and a sample of this mixture will be taken for chemical analysis."

The specifications on which the United States Government purchase state: "Samples of the coal delivered will be taken by a representative of the Government.... The sample taken will in no case be less than the total of 100 pounds to be selected proportionally from the lumps and fine coal, in order that it will in every respect truly represent the quantity of coal under consideration.

"In order to minimize the loss in the original moisture content, the gross sample will be pulverized as rapidly as possible, until none of the fragments exceed one-half inch in diameter. The fine coal will then be mixed thoroughly and divided into four equal parts. Opposite quarters will be thrown out and the remaining portions thoroughly mixed and again quartered, throwing out opposite quarters as before. This process will be continued as rapidly as possible until the final sample is reduced to such amount that all of the final sample thus obtained will be contained in the shipping can or jar and sealed air-tight."

In one instance, the Government found 46.23 per cent. ash in a sample of coal delivered to a public building. The contract was based on 4.78 per cent. ash, and they obtained samples as low as 6.70 per cent., while the average for 10 samples was 11.58 per cent. ash. Referring to this instance, Mr. Woodwell, in a paper before the American Society for Testing Materials, says: "Moreover, the coal passed the visual inspection of officers charged with the duty of checking the weights and of noting the presence of slate, dirt, etc."

The United States Geological Survey has analyzed and tested some "bone coal," and their analyses show only 45.43 per cent. ash in West Virginia 11-B and 28.08 per cent. ash in West Virginia No. 24.

The "bands" or streaks of "bone coal" found in the Pittsburg seam as mined in West Virginia contain only 25 to 30 per cent. ash. A sample of "bone coal" from Pennsylvania was found to contain 30.56 per cent. ash. It is very difficult to conceive that a coal higher in ash than "bone coal" would be delivered by any coal company, and still more improbable that any inspector would not

[1] Read before the Industrial Division of Amer. Chem. Soc., Baltimore, December 31, 1908.

detect the nature of such material from the most casual inspection. It seems more likely that such results were due to a non-representative sample.

Coal which undoubtedly did not vary more than 2 per cent. in actual quality was delivered under one of the other specifications, and the analyses show a variation of over 15 per cent. ash in individual samples.

In another instance, coal was delivered from one cargo to a state institution during two consecutive months, and one sample was accumulated throughout each month. The second sample showed over 20 per cent. more ash than did the first. This resulted in a penalty of over $1.50 per ton on all coal delivered for the month. The coal was all burned, so there was no chance to obtain a check sample, and the coal contractor had nothing to do but accept the reduced price, thus losing more than all the profit on the entire year's contract because of this one sample.

It is not strange that the coal companies are reticent about taking contracts on the analysis and heat unit basis, when they are at the mercy of non-representative samples. If there were only a corresponding error of sampling in the opposite direction, the results might average up very well in the end, providing a sufficient number of samples had been taken, but with a specified ash of 8 per cent., it is impossible to go 20 or 30 per cent. below the standard, while samples have shown this much above.

The impression seems to exist among many chemists, coal buyers and even coal companies, that the quality of coal from any one mine or region may vary a great deal more than is actually the case. The chemist may notice that certain results seem discordant and check the analysis, from his pulverized laboratory sample, and find that his analysis is correct. How many times does he check the taking and quartering down of the original sample? Here is where the discrepancies and inconsistencies are usually found; not in the quality of the coal itself or in the chemical analysis.

It is not intended to convey the impression that the quality of coal itself does not change, for it certainly is affected by the care of preparation, as well as local impurities which vary to some extent even in the same mine. It is because of these variations and the different quality and character of coal coming from different mines and regions that the coal is analyzed, but until the necessity of taking representative samples is realized by every one connected with the testing, buying and selling of coal, the errors in sampling will overshadow the variations in quality.

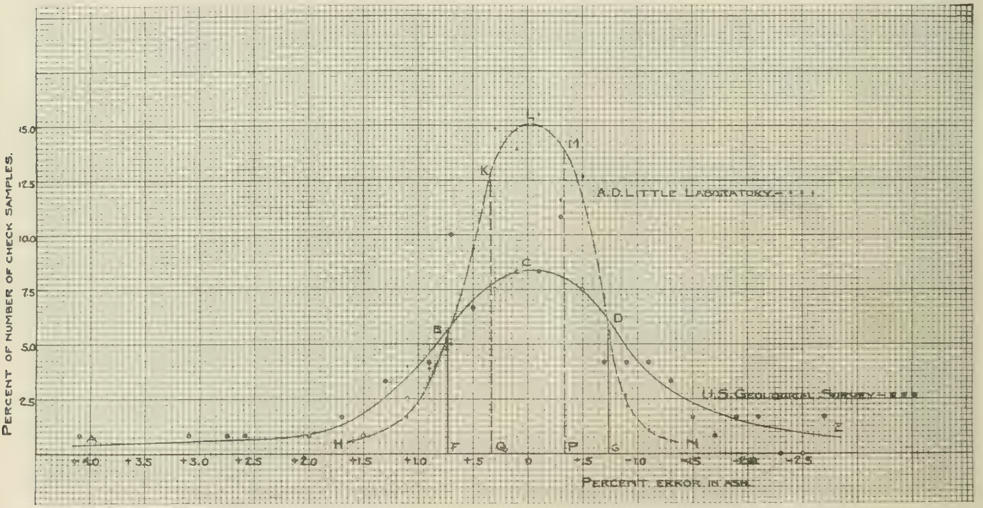


Fig. 1.

CAUSE OF ERRORS IN SAMPLING.

The word error as used here does not apply to

that class of analyses which have been so often used for advertising purposes and have been made from selected samples. It applies only to cases where two or more samples are separately taken from some one lot of coal of which each sample is supposed to be representative. The error of an individual ash determination is the difference between its percentage of ash and the average of all samples taken from the one lot of coal.

It has been found that these errors follow the probability curve so closely that the probable error of sampling by a certain method may be calculated by the method of least squares, just as the surveyor or physicist calculates the probable error of a number of observations or determines the limit of accuracy of a certain instrument.

Table I gives the errors on a large number of check samples from different sources.

areas A B H and E D N in the regions of greater error. The probable error in the two instances are represented by the distances O Q (0.33) and O F (0.73). This means that the area Q K L M P is equal to the sum of the areas H B K Q and P M D N lying outside of the probable error, or in other words, there are as many errors greater than 0.33 as there are less than this amount. The possible error or u, is the error that is likely to occur only once in 10,000 analyses, and would be represented on the curve as the point where the vertical ordinate is 0.01%. As this data follows the probability curve very closely, the formula for probable and possible error can be safely applied in determining the reliability of different methods of sampling.

In this table the last three columns, denoting the determined error and the calculated errors, are

Table I.

Actual Error and Probable Error in Percentage of Ash Resulting from Different Methods of Sampling Coal.

Item No.	Authority.	Weight of original sample lb.	Number of samples.	Lots of coal.	Average ash.	Maximum error by analysis.	Calculated. Probable error in ash r.	Calculated. Possible error in ash u.
1	Boiler tests by author	125	16	1	10.68	3.24	0.71	4.02
2	Pennsylvania Railroad Co., locomotive tests	60	17	1	7.83	3.52	1.21	6.19
3	Pennsylvania Railroad Co., locomotive tests	60	80	1	6.25	2.60	0.50	2.83
4	U. S. Geological Survey, car samples	100 to 800	120	34	10.17	4.10	0.73	4.16
5	U. S. Geological Survey, car samples, between 5% and 10% ash	100 to 800	48	13	6.71	2.06	0.56	3.19
6	U. S. Geological Survey, car samples, between 10% and 15% ash	100 to 800	64	19	11.88	3.11	0.76	4.34
7	A. D. Little Laboratory (all check samples)	600	181	56	8.28	1.58	0.33	1.86
8	A. D. Little Laboratory, under 10% ash	600	160	46	7.52	1.58	0.33	1.88
9	A. D. Little Laboratory, over 10% ash	600	21	10	11.78	0.93	0.30	1.68
10	A. D. Little Laboratory, sampled from vessel.	600	136	37	7.42	1.58	0.34	1.96
11	A. D. Little Laboratory, sampled from cars	600	18	7	10.02	0.93	0.33	1.88
12	A. D. Little Laboratory, sampled from piles	600	27	12	9.95	0.57	0.22	1.27
13	A. D. Little Laboratory, sampled from cars	250	62	8	7.98	1.61	0.41	2.36

No.	Original sample. Size.	Original sample. "Size-weight" per cent.	Broken to. inches	Quartered to.	"Size-weight" per cent.	Crushed to, inches.	Quartered to.	"Size-weight" per cent.	Pulverized to.	"Size-weight" per cent.
1	...	....	3/4	5 lb.	0.5	¼	50 grams	0.22	80–mesh	0.002[1]
2 and 3	..	....	"Almond"	5 lb.	...	....	½ lb.	....	....	....
4–6	1¼	0.23–0.03	½	25–50 lb	0.02–0.01	¼	2–10 lb.	0.01–0.002	60–mesh	0.005[1]
7–12	...	About 0.1	2–mesh	4 lb.	0.05	8–mesh	100 grams	0.012	80–mesh	0.002[1]
13	...	About 0.2	2–mesh	2 lb.	0.10	8–mesh	100 grams	0.012	80–mesh	0.002[1]

The results of items Nos. 4 and 7 have been plotted in Fig. 1. These curves involve no mathematics whatever, but represent the per cent. of analyses in which the errors fall between 0 and 0.2, 0.2 and 0.4, etc., both above and below the average. The significance of two probability curves plotted to the same scale, is that their areas are equal, and curve with the highest apex corresponds to the largest number of small errors. Whatever area B K L M D C one curve one may have above another near the zero axis must be equaled by the

given in percentages based on the coal as 100 per cent., and not on percentages of the amount of ash present in the coal. In each of these cases the average of all samples made on the same lot of coal was determined, and the error of each individual sample from this average was taken. The sum of the squares of each of these errors was substituted in the following formula:

$$(1) \quad r = 0.6745 \sqrt{\frac{\Sigma v^2}{n - 1}}$$

[1] Based on one gram sample taken from bottle for analysis.

"r" is the probable error.

"v" is the individual error.

"Σv^2" is the sum of the squares of the individual errors.

"n" is the number of samples analyzed to obtain the averages from which the errors were determined.

The formula used for calculating the possible error is:

$$u = 3.84\sqrt{\frac{\Sigma v^2}{n - 1}}$$

"u" represents the possible maximum error likely to be encountered once in 10,000 different samples.

The other symbols correspond to Formula 1, the only difference being the change in the constant.

The "size-weight" percentage referred to in the lower part of Table I is the percentage of the largest pieces of slate to the total weight of the sample previous to its last division or quartering. This ratio or percentage appears to be the most important factor to be considered in the sampling of coal.

Item No. 1.—Table I represents 16 samples taken from one car of Pennsylvania coal after it had been carted from the car and shoveled into a shed. During one boiler test when about three tons (including the samples), were taken from the pile, one shovelful was put into each of 16 barrels after every filling of the wheelbarrow. In this manner sixteen separate samples were accumulated, each consisting of one shovelful for each wheelbarrow-load taken from the pile, and any one sample should represent at least the three tons of coal taken from the bin, if this method of sampling is to be relied upon, and 125 pounds original sample is sufficient. This coal probably contained some pieces of slate weighing as much as one pound. These sixteen analyses are given complete in *American Society of Mechanical Engineers Transactions*, Vol. 27, page 636.

The data represented by Items 2 and 3, Table I, are taken from "Locomotive Tests and Exhibits" by the Pennsylvania Railroad System, Louisiana Purchase Exposition, 1904. This report states: "The coal finally selected came from the Scalp Level mines (near Johnstown, Pa.), owned by the Berwind-White Coal Mining Co." Some of this coal was also used by the U. S. Geological Survey at St. Louis and according to their reports the coal came from Eureka No. 31 mine.

The method of handling and sampling the coal used at the Pennsylvania Railroad testing plant, is given in their report as follows: "All coal was brought to the plant in low side gondola cars, and was shoveled over the sides of the car into boxes of a capacity of about 1000 pounds each. After dumping and before sprinkling, a small sample was taken and placed in a covered box....... About 60 pounds of coal were taken as a sample; this was crushed to the size of an almond and reduced by quartering to about five pounds. It was then ground fine and reduced to half a pound by further quartering, after which it was pulverized and a regular chemists' sample taken."

Each analysis given in this report is supposed to represent the coal used on a test, which varied from 1300 to nearly 15,000 pounds, averaging 6739 pounds. While the quality of coal used on any one test may not have been exactly the same, yet there can be no doubt but that 7,000 pounds taken from any part of the cars shipped from this mine would contain a more uniform ash than is shown by the analyses of the individual 60-pound samples. A careful study of these results shows that there is no apparent relation between the variation in ash and time, as the results of consecutive tests show great variations, for instance, 7.25, 11.35, 7.63 per cent. ash. Averaging the different series of tests the ash is 7.83, 6.30, 6.10, 6.23, 6.31, 6.27, 6.25, and 6.30, indicating that after the first series of tests the quality of coal itself ran remarkably uniform. It appears that the coal received subsequent to the first series of tests had been better prepared, as the ash averages about 1.5 per cent. less. The errors are greatly reduced, indicating that the amount of slate and impurities has a great deal to do with the accuracy of sampling in addition to the "size-weight" per cent.

The data for Item No. 4 was taken from Professional Paper No. 48 of the United States Geological Survey and includes all analyses made of the different car samples taken at St. Louis during the period covered by this report. These results have been tabulated on pages Nos. 281 to 284. The errors have been determined from the average of all plant samples as a basis, which is probably not absolutely correct, considering the fact that the car samples were taken by a different method than were the samples from the steam, coke and gas plants—the principal difference being in the size of the initial sample. The car samples consisted of from 200 to 800 pounds orig-

inal sample, while the samples taken from the gas plant were said to weigh about 100 pounds. This report also states that the samples from the steam plant were collected in galvanized iron cans which were about 18 inches in diameter and 30 inches high. On this basis, the capacity of these cans would be a little over 200 pounds; but it is not stated whether or not these cans were completely filled during each test. Apparently no mention has been made of the quantity of coal taken from the original sample in the coke plant.

From these various plants, the samples were quartered down by the conical pile method to 50 or 25 pounds and were then turned over to the chemical laboratory, where they were further reduced in size and quantity, as indicated in the lower part of Table I. All of this coal had been crushed to about 1¼ inches previous to any of the samples being taken.

Mention is made in several of the recent publications of the United States Geological Survey that there is a decided tendency for the heavier pieces, such as slate and pyrites, to settle to the bottom of the car. If this is true, it is probable that some of the errors here indicated may be somewhat greater than was actually due to the sampling. However, the same tendency holds true in the case of the other sets of samples presented in this table, and the comparison is undoubtedly justified.

Items Nos. 5 and 6 include the same data as is represented by Item No. 4, except that the results have been classified according to the average ash content in the various coals. It is noted from this comparison that the probable error in the coals containing between 5 and 10 per cent. ash is 0.56 per cent., while it is 0.76 per cent. ash in the coals containing over 10 and less than 15 per cent. ash.

Item No. 7 includes all of the check samples which have been made in a commercial laboratory during the past year. One hundred and eighty-one samples from 56 different lots of coal are represented. In these 56 different lots, there were only 14 varieties of coal included. The different lots represent either individual vessel cargoes, carloads or piles. It is noted that the maximum error found in these 181 samples is 1.58 per cent., while the probable error of each individual sample is 0.33 per cent.

Items Nos. 8 and 9 give the same analyses classified as to percentage of ash, and it is noted that there is practically no difference.

Items Nos. 10, 11 and 12 give the same analyses classified as to vessel, car and pile samples, and it appears that the probable error is less in the latter case than in the vessel and car samples, which are practically the same.

Item No. 13 includes 62 samples which have not been included in any of the above items. This coal was discharged at tide-water and loaded into railroad cars. A wheelbarrowful was taken from each car of coal as it was received at the plant, from which a sample was worked up and analyzed. The eight different lots indicate the number of cargoes received, while in fact there were only three kinds of coal and 42 of these analyses were made on one kind only. The averages of the five or more samples from each different cargo of this one coal varied only 0.8 per cent.

The important point brought out by Table I is the decreasing error with the larger original samples. For instance, the comparable cases where the writer was personally familiar are Items 1, 11 and 13.

Item.	Wt. original sample, lbs.	Actual error.	Calculated possible error.
1	125	3.24	4.02
13	250	1.61	2.36
11	600	0.93	1.88

Likewise, the results from such reliable laboratories as the Pennsylvania Railroad and United States Geological Survey show similar error when only 60 and 100 pounds have been taken as original samples. It should be understood that the car samples taken by the Government have probably been as well or even better taken than those from Little's laboratory; but the wide range of error is undoubtedly due to the samples from the steam, gas and coke plants, where only 100- to 200-pound original samples were taken.

EXPERIMENTAL SAMPLING.

After realizing the importance of keeping the ratio of the largest pieces to the weight of the sample, or the "size-weight" per cent. low, a series of experiments was made in order to determine how the variation in percentage of ash was affected by this ratio. The coal selected was a Pennsylvania semi-bituminous coal which was known to contain about 5 per cent. of ash in the form of slate and impurities in addition to the intrinsic ash of the coal itself. This coal contained very little pyrites or sulphur, as indicated by the following analysis:

Moisture	0.56%
Volatile	15.86%
Fixed carbon	72.08%
Ash	11.50%
Sulphur	0.93%
B. T. U.	13791

About 29 pounds of this coal were taken originally, and all of it was put through a 2-mesh sieve. It was then "quartered" or divided by means of a riffle sampler; this was repeated until about 144 grams remained to be divided. This remaining amount was divided and one-half (72 grams) of it was pulverized to 80-mesh and put into a bottle; the other half of this, instead of being returned with the large part of the original sample, was divided, making two 36-gram samples, one of which was pulverized to 80-mesh and bottled, while the remaining 36 grams were divided again, and one of the 18-gram samples pulverized, while the other was returned to the original sample. The original sample was again divided in the same manner and the complete operation repeated five times, thus giving five 72-gram, five 36-gram and five 18-gram samples. The remaining original sample was then screened through a 4-mesh sieve, and all that was too large was broken in a mortar until all of it passed through 4-mesh. Fifteen more samples were obtained from this coal in the same manner employed to get the fifteen 2-mesh samples. All of the remaining original sample was then put through an 8-mesh sieve and the entire operation repeated and carried one step further, making twenty 8-mesh samples, five each weighing about 72, 36, 18 and 9 grams.

A second and third series of samples were also obtained from the remaining original 8-mesh sample, but the second series was carried down to a 1-gram sample, and the third series was divided down to a 0.3-gram sample. In the third series, the samples of 2 grams and smaller were divided by quartering on glazed paper with a spatula; all other divisions were made with the riffle sampler. The samples of 2 grams and less were not pulverized, but the entire amount of coal contained in them was weighed up and burned in platinum crucibles.

The fourth series, consisting of ten 144-gram samples, was later made from the original sample, and from each of these 80-mesh bottle samples ten grams were taken and a composite sample mixed. Ten analyses were made from this one composite sample, after which it was further pulverized in an agate mortar until it all passed through a 200-mesh sieve. Eleven more analyses were then made from this sample. In all there were 193 samples made from this one original 29 pounds of coal.

The phase of sampling which is particularly considered in this paper is the percentage of ash, consequently the ash only was determined from each of these samples, excepting a proximate and B. T. U.

TABLE II.

ASH DETERMINATION WITH DIFFERENT "SIZE-WEIGHT PERCENTAGES."

Weight of sample gram	Composite	Composite	144	72.1	35.2	17.15	8.85	73.0	4.52
All through sieve before dividing	...	...	8-M	8-M	8-M	8-M	8-M	4-M	8-M
"Size-weight" per cent	0.0002[1]	0.0014[1]	0.00835	0.0167	0.0341	0.070	0.136	0.150	0.266
Pulverized to	200-M.	80-M.	80-M.	80-M.	80-M.	80-M.	80-M.	80-M.	80-M.
Ash per cent	...	...	...	...	...	...	...	...	10.21
	...	...	...	...	...	...	...	...	10.60
	...	...	...	11.08	12.06	11.96	11.58	...	10.76
	...	...	...	11.58	12.10	11.06	11.04	...	10.48
	...	...	...	11.78	11.92	12.30	11.28	...	11.64
	...	...	...	11.72	12.16	12.14	11.88	...	11.74
	11.50	...	...	11.82	12.04	12.60	11.10	...	11.22
	11.50	11.34	11.38	11.24	11.20	11.30	12.06	...	11.33
	11.48	11.48	11.28	11.68	12.02	12.04	11.46	...	11.40
	11.54	11.62	11.78	11.20	12.06	12.70	11.04	...	11.33
	11.48	11.50	11.46	11.52	11.08	11.90	12.44	...	11.20
	11.46	11.48	11.38	11.30	11.88	11.66	11.54	...	10.27
	11.54	11.40	11.30	11.64	11.30	11.18	11.26	11.98	12.32
	11.48	11.36	11.16	11.66	11.26	11.26	11.52	12.32	11.28
	11.50	11.60	11.00	11.10	11.36	10.66	11.58	11.95	11.40
	11.54	11.40	11.16	11.48	10.90	12.06	11.44	12.30	11.32
	11.48	11.42	11.40	11.04	10.98	11.34	10.80	12.16	10.32
Average	11.50	11.46	11.33	11.46	11.62	11.68	11.47	12.14	10.65
Maximum error from 11.50	0.04	0.16	0.34	0.46	0.66	1.20	0.94	0.82	1.29
Error of average from 11.50	0.00	—0.04	—0.17	—0.04	+0.12	+0.18	—0.03	+0.64	—0.85
Calculated									
r or probable error	0.02	0.07	0.18	0.19	0.33	0.43	0.34		0.58
u or possible error	....	0.40	1.04	1.05	1.87	2.48	1.91		3.28

[1] Based on one gram taken from bottle for analysis.

TABLE II.—(*Continued.*)

Weight of sample gram	36.4	2.2615	18.2	1.1368	71.8	0.5867	35.5	0.3001	17.8
All through sieve before dividing	4-M.	8-M.	4-M.	8-M.	2-M.	8-M.	2-M.	8-M.	2-M.
"Size-weight" per cent	.305	0.53	0.61	1.06	1.16	2 045	2.35	4.00	4.65
Pulverized to	80 M.	Not pulverized.	80 M.	Not pulverized.	80-M.	Not pulverized.	80-M.	Not pulverized.	80 M.
Ash, per cent	...	...	...	10 47	...	...	...	...	...
	...	...	...	11.39	...	...	...	...	...
	...	...	...	9 74	...	..	..	...	...
	..	...	...	9.37	...	..	...	...	...
	...	...	..	10.45	...	...	...	...	...
	...	10.91	...	10.29	...	...	...	...	...
	...	9.57	...	12.41	...	...	..	...	...
	..	10.37	...	9 32	...		.	...	...
	..	10.88	...	10.06	...		.	...	...
	...	10.40	...	10 80	...		...	...	...
	..	11 22	...	10.39	...	10 73	...	10.79	...
	...	12.13	...	11 30	...	12.79	...	10.66	...
	...	11.23	...	12.79	...	13 50	..	13.48	...
	...	10.20	...	10.11	...	9.14	...	12.18	...
	...	9.61	...	11.34	...	10.77	.	15.86	...
	11 64	11.49	11.64	12.09	11 88	10.06	11.68	11.52	15.56
	12.92	10.55	11.84	12.97	10.50	9.74	14.12	8.71	9.76
	10.76	11.55	10.70	9.72	13.80	12.01	11.72	9.58	8.84
	10.82	12.20	11.74	10.30	12.10	11.21	11.20	13.32	12.78
	12.48	10.92	11.76	7.60	11.24	11.91	11.36	8.95	9.18
Average	11.72	10.88	11.54	10.65	11.90	11.19	12.01	11 50	11 22
Maximum error from 11.50	1.42	1.93	0.80	3.90	2.30	2.36	2.62	4.36	4.06
Error of average from 11.50	+0.22	—0 62	0.04	—0.85	+0.40	—0.31	+0.51	0 00	—0.28
Calculated									
r or probable error		0.60		1.01		0.90		1.65	
u or possible error		3.41		5.72		5.14		9.40	

determination that was made from the 200-mesh composite sample. In every case the coal was burned to ash in platinum crucibles placed in a gas muffle.

Each ash determination made is given in Table II and arranged in columns according to the "size-weight" per cent. The percentages of ash in each column are in order as determined. The average of the eleven 200-mesh composite ash determinations has been taken as representing the true average ash contained in the coal as it was taken from the ten 144-gram, 8-mesh samples after they had been pulverized to 80-mesh. It is noted that the maximum error of individual samples from the true average of 11.50 gradually increases with the "size-weight" per cent. The probable and possible errors have been calculated according to formulas (1) and (2), and these values also increase with the increasing percentage of the largest piece to the weight of sample. It will be noted that the probable error of taking one-gram quantities out of the 200-mesh sample is 0.02 per cent. This is probably the limit of accuracy of weighing on the balance, as a 12-milligram rider is used and it is customary to weigh no closer than 0.2 milligram, consequently no possible error was calculated in this instance.

Had the importance of obtaining a large number of results been fully realized at the start, the work would have been more concentrated, especially with the larger "size-weight" percentages, which would have resulted in a more uniform increase in the individual errors, as well as the values calculated for "r" and "u."

This work might be criticized by some because of its being carried out on a comparatively small scale, but when the results compare as favorably as they do, whether 2-mesh samples weighing 17.8 grams or 8-mesh samples weighing only 0.3 gram are used, as noted in the last two columns of Table II, there can be little doubt that it would hold true from the largest sizes of commercial coal down to a sample as small as 200-mesh.

It will be noticed from these ash determinations that even in cases where the "size-weight" per cent. is comparatively high and variations of over 5 per cent. occur in ten or more analyses, there may be cases where three or more consecutive determinations agree within 0.50 per cent. Too often have chemists supposedly determined their range of error by making only a few check determinations. Two analyses or check samples are of little value in arriving at the limit of accuracy in any case; ten checks are not conclusive, but it would be better to repeat the determination 50 or 100 times at least.

In Fig. 2 the results of Table II have been plotted in terms of "size-weight" percentage and per-

centage of ash. The analyses given in the first and third columns are left out because of the impossibilty of putting so many points in such a small space. Also, the results of the second column are indicated by two short horizontal lines extending to the left of the vertical axis and represent the extremes only. The lines showing the limits of the plus and minus errors have been drawn evidently one in ten thousand and probably would not have been approached again even had a thousand samples of this class been analyzed.

The points with large circles connected by a broken line represent the average ash of each set and are found both above and below the true average line, with some surprising variations.

The lower full line curve of Fig. 2 represents

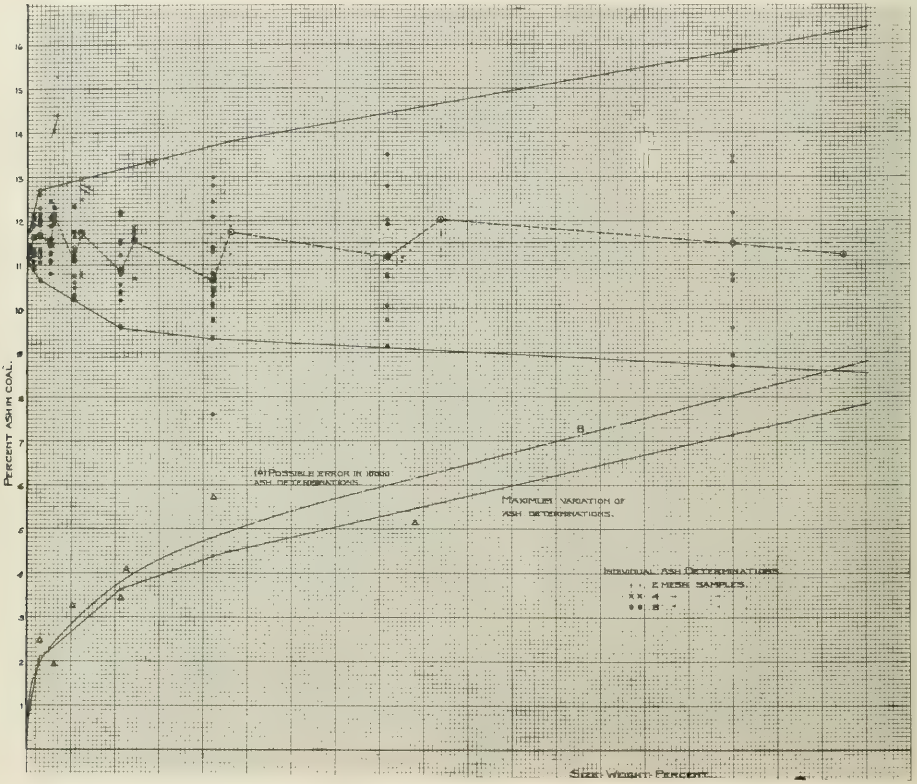


Fig. 2.

through the exterior points of the various sets of analyses, connecting the greatest errors, rather than in and out, as it would necessarily have had to be drawn in some instances where too few results were determined under one set of conditions. One exception had been made in the instance of the 7.60 per cent. ash on a sample where the "size-weight" per cent. was 1.06. This one point is the variations in the individual analyses plotted from the horizontal axis.

The triangular points are plotted from ("*u*") the possible error in 10,000 as given at the bottom of Table II.

The curve A B has been drawn with respect to these points, giving some weight, also, to the nature of the variation curve as actually determined.

This possible error curve represents the error from the average only, while the determined variation curve is the sum of the plus and minus errors. Had more determinations been made in the several cases, the possible error or ("u") points would undoubtedly have fallen more consistently.

From these results, it will be at once realized that the "size-weight" per cent. should be less than 0.1 per cent., if errors of 2 per cent. are not to be exceeded or the probable error is to be less than 0.4 per cent. ash with a coal that contains about 5 per cent. ash in the form of slate and foreign impurities when quartered.

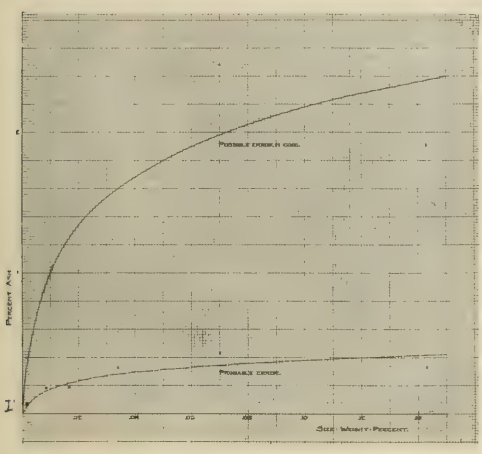


Fig. 3.

Fig. 3 gives the possible error curve from Fig. 2 drawn to a larger scale, and according to this, the "size-weight" per cent. must be as low as 0.01 per cent. if an error of 1 per cent. in ash is not to be exceeded. Even with this small ratio, the probable error is almost 0.2 per cent.

APPLICATION OF THE LAW OF PROBABILITY.

Fig. 2 shows that the error does not increase directly with the "size-weight" per cent., but it rises very rapidly from the origin, making a curve similar to a parabola. When the "size-weight" per cent. is 0.5 per cent., the determined variation in ash is 3.5 per cent., or seven times the variation due to an odd piece of slate going into one sample one time and into another the next. It, therefore, indicates that it is not a question of one piece of slate or high ash coal that causes the error, but several individual pieces which, according to the law of chance, fall more on one side than on the other.

In order to determine the extent of this variation, a series of experiments was made as follows: Sixteen small pieces of coal (4-mesh) were placed in a can containing a quantity of sand and the mixture divided in the riffle sampler. The number of pieces of coal falling on the right-hand side of the sampler were counted, and this half divided again, and the operation repeated until no coal fell on the right-hand side. Theoretically each division should have halved the number of pieces of coal, giving 8, 4, 2, 1, 1 or 0 for the successive divisions, but out of 100 times there were only two sets of divisions where these conditions were fulfilled, and from 100 sets of similar divisions with 32 pieces of coal, corresponding conditions were not fulfilled at all. Some of the results obtained were:

After 1st	2nd	3rd	4th	5th	6th	7th	8th Division.
4	3	0					
11	8	6	3	2	2	1	0
7	2	1	1	0			
9	5	3	2	0			
12	4	1	1	1	0		
8	5	5	0				

After 100 such sets of divisions had been made with both 16 and 32 pieces of coal, it was realized that the first division of each set was of the greatest importance, and that a large number of separate divisions was necessary to determine the law governing the error; consequently 1300 divisions were made, using 8, 16, 32, 64 and 128 pieces. With a fewer number of pieces—four, for instance—it took only a few divisions before the extreme possible variation was reached, *viz.*, either getting 4 or 0 pieces on the right side from the first division.

While the riffle sampler is pretty well known, it might be well to describe the one used in this work. It consists of a series of 20 troughs ½-inch wide, made of tin and soldered together so that each adjacent one slopes in the opposite direction at an angle of about 30 degrees from vertical. The sampler is put over the sides of two rectangular cans setting close together, and the sample to be divided is poured from a similar can on to the tops of the 20 troughs. The top edges of these troughs are level, so that the flat stream of coal falling on the sampler is divided into 20 streams ½-inch wide. Each alternate twentieth part of the entire sample goes into one of the collecting cans, while the other can receives the other half. In dividing

down a sample of coal for analysis, the sample may be divided several times, resulting in ½, ¼, ⅛, etc., of the original until the sample is reduced to the desired quantity. The term dividing has been used in preference to "quartering," because in this case the sample is in reality divided into 20 parts instead of four.

The results of the several hundred divisions made of the different numbers of counted pieces of coal are given in Table III.

Table III.

Results of Counting Marked Pieces of Coal after Being Divided on a Riffle Sampler.

1 Number of pieces coal (n)	**4**	**8**	**16**	**32**	**64**	**128**
2 Times divided	58	100	200	300	400	300
3 Theoretical number after division	2	4	8	16	32	64
4 Average of all divisions, pieces	1 86	3 92	8.04	16 61	32.33	65.88
5 Per cent. above or below item 3	—3 5	—1 0	+0.3	+1.9	+0 5	+1.5
6 Smallest number pieces found	0	1	3	9	21	47
7 Largest number pieces found	4	8	12	23	43	80
8 Maximum variation. Number pieces	4	7	9	14	22	33
9 r of probable error—formula (1)	....	0.91	1.17	1.67	2.61	3.79
10 u or possible error—formula (2)	....	4.00	6.63	9 51	14.90	21.80
11 u' or possible error from empirical formula (3)	....	3.94	6 40	9 88	14.80	21.77
12 Per cent Item (11) to Item (1)	....	49.3	40 0	30.9	23.2	17 0

From Items 4 and 5 it will be noted that the averages of all divisions are reasonably close to the theoretical average.

The important item in this table is 8, or the maximum variation in the number of pieces of coal falling on one side of the sample at different times as compared with the total number of pieces in the sample divided. The data from these divisions make it possible to plot very good probability curves, as seen in Fig. 7.

Items 9 and 10 have been calculated by substituting the individual errors of the several hundred divisions in formulas (1) and (2), which have been previously explained and used in calculating the probable and possible errors of the commercial samples. Item 9, after being divided by two in order to change it from variation to error, has been plotted in Fig. 4 as "maximum error found." The probable error as well as the probable error in 10,000 determinations have been plotted to the same scale.

From the possible error curve as plotted in Fig. 4, it appears that this curve is similar to a parabola, conseqeuntly a formula has been derived by substituting the different values of u and n from Items 1 and 10, Table III, in the formula

$$u = a + b\sqrt{n}$$

and solving for the constants a and b by the method of least squares. This results in formula

$$u = 2.10\sqrt{n} - 2.01. \quad (3)$$

Where u is the possible error in number of pieces above or below the average, n is the number of pieces of coal contained in the sample before it is divided.

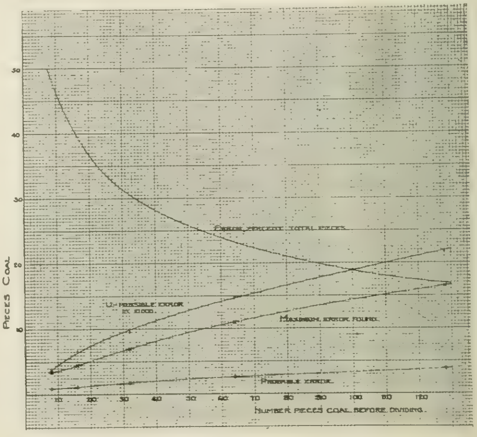


Fig. 4.

It is noted from Item 12 and the curve on Fig. 4, plotted from these results, that in spite of the increasing error in the number of pieces with the greater number of pieces divided, the percentage of error to the total number of pieces divided grows less. From this fact, together with formula (3), we readily see that in the case of sampling coal the important point lies in the number of pieces of slate, bone or coal having higher than the average percentage of ash. If a certain lot of coal contains a certain percentage of ash in the form of slate, etc., the error in sampling will be greatly diminished as the pieces of slate are broken finer and the number of them thereby increased. It seems reasonable to assume that the weight of the average piece of slate in a sample of coal would be about one-half that of the largest pieces, although this might be greater or less, depending upon how the sample was broken up.

If a = per cent. ash due to slate, free impurities, etc., in sample to be divided

p = "size-weight" per cent. or per cent. of largest pieces of slate in sample to be divided

n = number of pieces of slate, or equivalent, in sample to be divided

u = error possible to occur once in 10,000 pieces of slate after dividing

e = error possible to occur once in 10,000, per cent. ash to sample after dividing

r = probable error, per cent. ash to sample after dividing.

Assume $p/2$ = weight of average piece of slate or equivalent,

then $a = np/2$ and $n = 2a/p$

also $e = 2\,up/2$ and $e = up$.

Now as $u = 2.10\sqrt{n} - 2.01$ (formula 3) by substituting this value of u and the value of n in the formula

$e = up$ we have

$e = p\,(2.10\sqrt{2/p} - 2.01)$ or

(4) $e = 2.97\sqrt{ap} - 2.01\,p$

The maximum error likely to occur one time in 10,000 is 5.7 times greater than the probable error, therefore

(5) $r = 0.522\sqrt{ap} - 0.353\,p$

From these formulas it is apparent that the error in sampling is dependent upon the percentage of ash in the form of slate, etc., and the "size-weight" percentage, and by assuming different values for a and p the possible and probable errors have been calculated and plotted in Fig. 5.

Curve "AB" from Fig. 2 has also been plotted in Fig. 5 to the same scale, and it is noted that it follows the 5 per cent. ash calculated error curve very closely excepting where the "size-weight" percentage is below 0.2 per cent. Even here, the curves are of the same general nature and rise very abruptly from the origin, indicating that in order to keep the error within any reasonable limits, the "size-weight" percentage must be very small.

It is very reasonable to expect that the possibility of error would increase with the percentage of ash existing in the sample as slate and other such impurities. It does not follow that the error is necessarily greater in sampling a high ash coal as compared with a low ash coal, for if the coal contains a high intrinsic ash it is already more or less uniformly mixed throughout the coal. It is the difference between the total ash in any given lot of coal and the intrinsic ash, or that contained in the purer lumps of coal, which affects the error of sampling for any given size and weight of sample to be divided.

The difference in the percentage of ash in car samples and mine samples is a very good indication of the amount of ash that causes the variation in sampling.

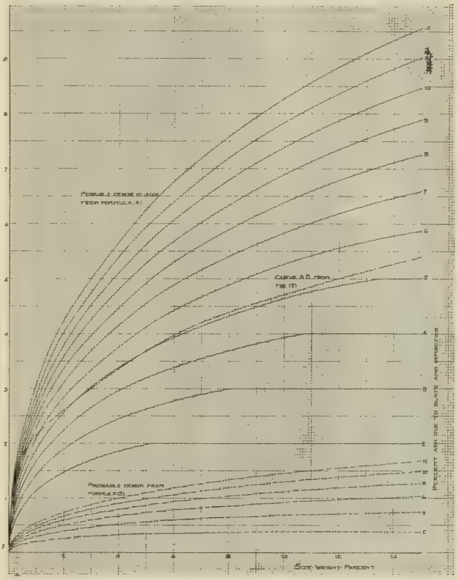


Fig. 5.

In Bulletin 316 of the United States Geological Survey, Mr. Burrows has compared the ash in mine samples with the ash in the run of mine, screened coal and slack shipped under inspection from the corresponding mines.

From 87 mines the average ash in the run of mine samples was 2.67 per cent. higher than in the corresponding mine samples. In the 67 cases of screened coal being loaded, the ash averaged 3.06 per cent. higher, and from 15 slack samples the ash was 5.97 per cent. higher than in the corresponding

mine samples. In several individual instances the ash in the car samples was more than 10 per cent. higher than in the mine samples.

United States Geological Survey Bulletin 323 also gives data bearing on this point. On pages 30 to 35 the results of washing 23 different coals in a solution of 1.35 specific gravity are given, and the difference between the ash in the original sample and that part of the coal which floated in this solution was 4.75 per cent. In several instances the difference exceeded 10 per cent. ash.

While the ash due to slate and impurities may vary from less than one per cent. to over 10 per cent. in commercial coals, the average appears to be somewhere near 3 per cent.; but considering the number of instances where the difference is greater than this amount, it seems advisable to assume 5 per cent. for this value, as it cannot be determined in individual cases very readily, and in no case will it be definitely known before the sample is taken.

Of the 23 coals washed in the 1.35 specific gravity solution, only three contained over 7 per cent. ash in the washed coal, and in some cases this intrinsic ash is as low as 1.52 per cent.

In Bulletin 316, Mr. Burrows also classifies the sample of run of mine coal according to the ash in the mine samples. In the case of 35 coals, where the ash in the mine samples was less than 7 per cent. (averaging 4.80), the car sample contained 2.97 per cent. more ash, while with the 47 samples, where the ash in the mine samples was more than 7 per cent. (averaging 9.50), the car samples showed only 2.69 per cent. more ash than did the corresponding mine samples. This indicates that the total ash is no indication whatever of the amount of ash existing as slate, etc. It is largely dependent upon

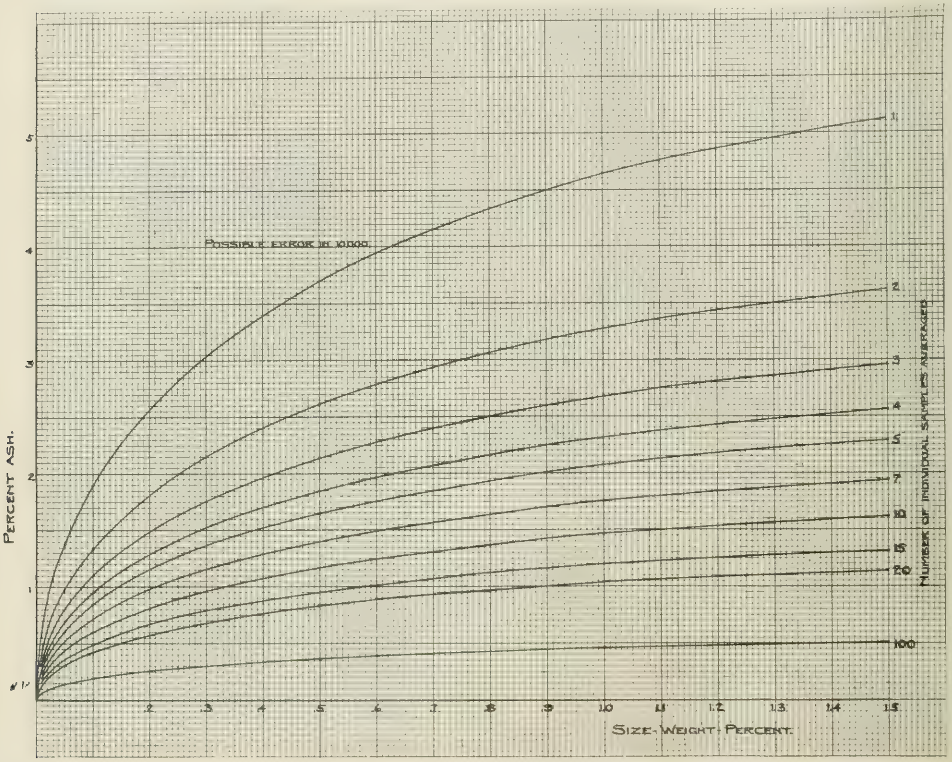


Fig. 6.

the nature of roof, floor and partings found with any seam of coal, together with the care in mining and preparation of the coal. The percentage of slate and free ash increases as the sample is broken and crushed to the smaller sizes, as the breaking frees thin streaks of slate, bone and pyrites from the lumps of coal to which they may have been attached in the original sample.

Throughout all of the experimental work presented in this paper, the dividing of the samples was done on the riffle sampler, but two samples of coal containing 16 and 32 pieces of coal, painted white, were each mixed and quartered 100 times by means of a spatula, and the number of pieces of

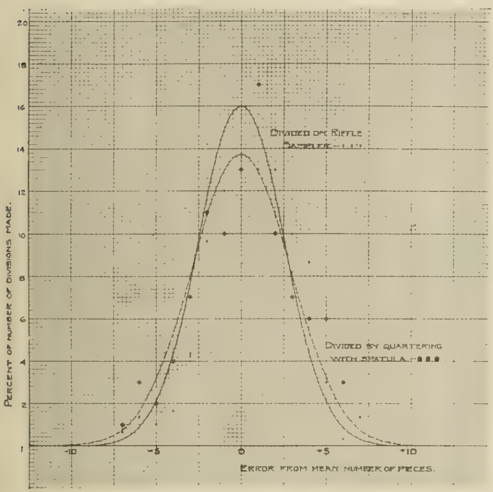


Fig. 7.

white coal in each quarter were counted. From the variation in the sums of the number of marked pieces in the two opposite quarters, the probable error was calculated. A probability curve was drawn from the 32-piece sample and shown in Fig. 7 in comparison with the probability curve from 300 divisions of 32 pieces with the riffle sampler. It will be noted that there seems to be a little greater error by the quartering method. The pieces of marked coal in two adjacent quarters were also added, and from the results obtained the discarding of two opposite quarters seems to give little, if any better results than if the conical pile had been simply halved. However, this phase of sampling was not investigated with sufficient thoroughness for any definite conclusions to be drawn.

AVERAGE OF ANALYSES.

Many laboratories have realized the large errors likely to occur in individual samples and have attempted to obtain the true quality of any lot of coal by taking several duplicate samples and averaging the results of the several separate analyses.

According to the law of averages, the probable error of the average of any number of observations is expressed by $r_o = r/\sqrt{n}$ where r is the probable error of the individual observations and n is the number of observations averaged; so the probable error of the average of four samples is only one-half the probable error of the individual samples, providing the same method has been used in taking each sample. The same is true of the possible error.

From the 1300 divisions and counting of the number of pieces of coal, the results were averaged by twos, fours, sixes, eights, tens, etc., and the probable error of the averages determined. It was found that the above formula held true to within reasonable limits, hence it was used in calculating the values which have been plotted in Fig. 6. This set of curves is the same as the curve of Fig. 5 obtained from formula (4), where $a = 5$ per cent., except the values of e for corresponding "size-weight" percentages which have been divided by the square root of the number of samples averaged.

This set of curves indicates that if the possible error is to be less than one per cent., the "size-weight" percentage must be less than 0.024 per cent. if one sample only is taken, while if 10 samples are taken the "size-weight" percentage may be 0.33 per cent. in each sample and still be assured that the possible error will be only one per cent. In order that these conditions may be fulfilled, the one sample should be 13.7 times larger when originally taken from the lot of coal than is each of the 10 samples. The result would be that 27 per cent. less coal need be taken and broken up for the original 10 samples than in the one individual sample. Similarly, 47 per cent. less coal need be taken originally, providing it is divided into 20 separate samples. As the greatest difficulty is in taking and quartering down the original sample, it might often be better to take several original samples, and to mix them after they have been quartered down to a comparatively small size, making one sample for the final pulverizing and analysis.

WEIGHT OF VARIOUS SIZES OF COAL AND SLATE.

In order to determine the weights of the largest pieces of slate that would pass through different sizes of bar screens and sieves, pieces of both slate and coal were weighed for the different sizes from 4-inch screen to 80-mesh per inch sieves. The results are given in Table IV. On account of the few pieces of slate larger than 2-inch screen, their weights are rather discordant when compared with the weights of coal of the same size, consequently, in plotting Fig. 8 it was assumed that for sizes larger than 2½ inches the weight of the slate was 2.25 times that of the coal. The specific gravity of the coal, slate and pyrites was determined as follows: Coal, 1.36; slate, 2.55; pyrites, 4.28; thus making the ratio of the specific gravities of slate to coal 1.87: 1. It is noted from Table IV that the ratio of the weights of slate to coal is greater than this in each case, where a sufficiently large number of pieces were weighed, until they were broken to 8-mesh. This is probably due to the slate usually occurring in the form of flat pieces; and in breaking the slate it tends to form long, slender pieces rather than cubical, as does the coal; while the pyrites may exist in more or less lens-shaped pieces, yet in breaking it forms more nearly cubical pieces, so that its weight was taken as 3.15 times the weight of the different sizes of coal. The ash or iron oxide resulting from the

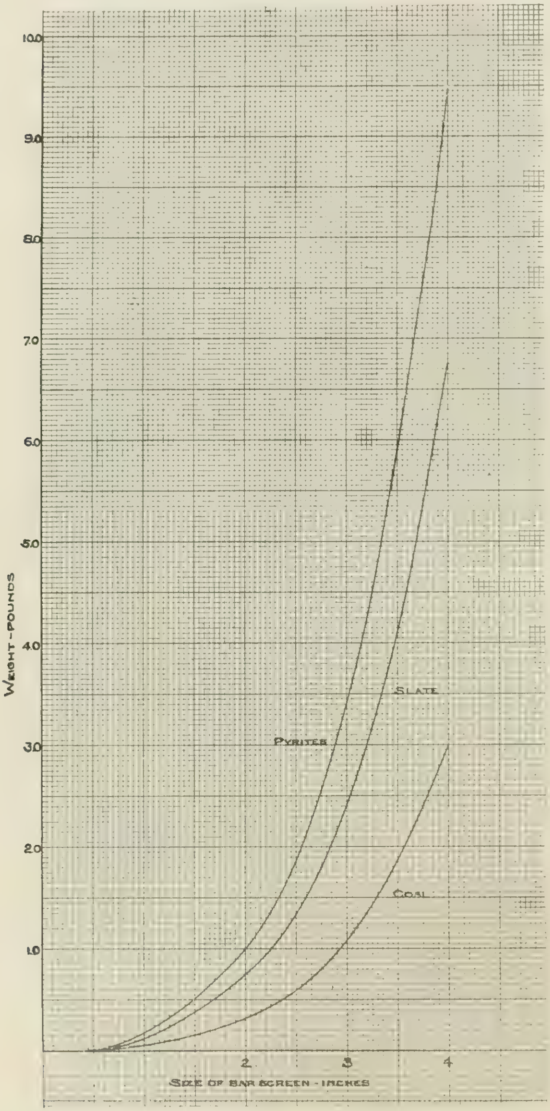


Fig. 8.

TABLE IV.

WEIGHT OF COAL AND SLATE THROUGH BAR SCREENS AND SIEVES.

		Slate		Coal.		
Through.	Over.	Number pieces weighed.	Average weight per piece. Lbs.	Number pieces weighed.	Average weight per piece. Lbs.	Ratio average weight of slate to coal.
4	3½	2	3.8	6	2.4	1.58
3½	3	2	1.97	6	1.43	1.38
3	2½	5	1.24	16	0.806	1.54
2½	2	5	0.98	23	0.435	2.25
2	1½	14	0.553	47	0.236	2.35
1½	1	51	0.240	138	0.106	2.26
1	½	152	0.0463	648	0.0195	2.37
½	2-mesh	238	0.0076	601	0.00368	2.06
Mesh.	Mesh.		Gram.		Gram	
2	4	108	0.805	597	0.340	2.37
4	8	1057	0.0899	702	0.428	2.10
8	10	592	0.0168	643	0.00898	1.87
10	20	931	0.0036	1069	0.001925	1.87
20	40	770	0.000201	....	....	....
40	60	1000	0.0000606	....	...	....
60	80	2000	0.0000257	....	.....	...

burning of pyrites is a little more than that due to a piece of slate of corresponding size.

Some of the slate used for these experiments was found to lose 11 per cent. upon being heated in the muffle. Figs. 9 and 10 give the weights of different sizes of coal and slate between 2-mesh and 80-mesh from Table IV. In Fig. 9 the results are plotted to nominal sizes of sieves, but Fig. 10 takes account of the actual size of the openings. The lengths of the sides of the larger openings were measured with a microscope in the sizes from 20 to 200-mesh.

Sieve. Mesh.	Length of side. inch.
2	0 425
4	0.25
8	0.10
10	0.076
20	0.0358
40	0.0164
60	0.0134
80	0.0089
100	0.0060
200	0.0030

The weights of the various sizes of coal, slate or pyrites can be read from the curves of Figs. 8 9 and 10, which have been drawn through the points of average weight. In several instances the largest pieces were weighed up separately and usually were a little higher than the results read from the curves for corresponding sizes.

WEIGHT AND SIZES OF SAMPLES.

From the foregoing data we are enabled to take and quarter down a sample of coal and be assured that the possible error may be within certain required limits. While accuracy of 0.25 per cent. would be desirable, it is seen from Fig. 3 that in order to be certain that errors would not exceed this amount, the "size-weight" percentage must be 0.001 per cent. In sampling run of mine coal, where pieces of slate weighing 5 pounds are often encountered, the original sample would have to consist of no less than 225,000 pounds; or if the coal had been previously crushed to 2 inches, the original sample should contain 37,000 pounds. Samples of this size are practically out of the question considering the expense necessarily involved as compared with the value of the material being sampled.

Any sample, however, should be within one per cent. of the true ash, in which case the probable error would be 0.18 per cent.; and from Fig. 3 the "size-weight" percentage should be 0.01 per cent. in order that this degree of accuracy would be assured. The "size-weight" percentage is based

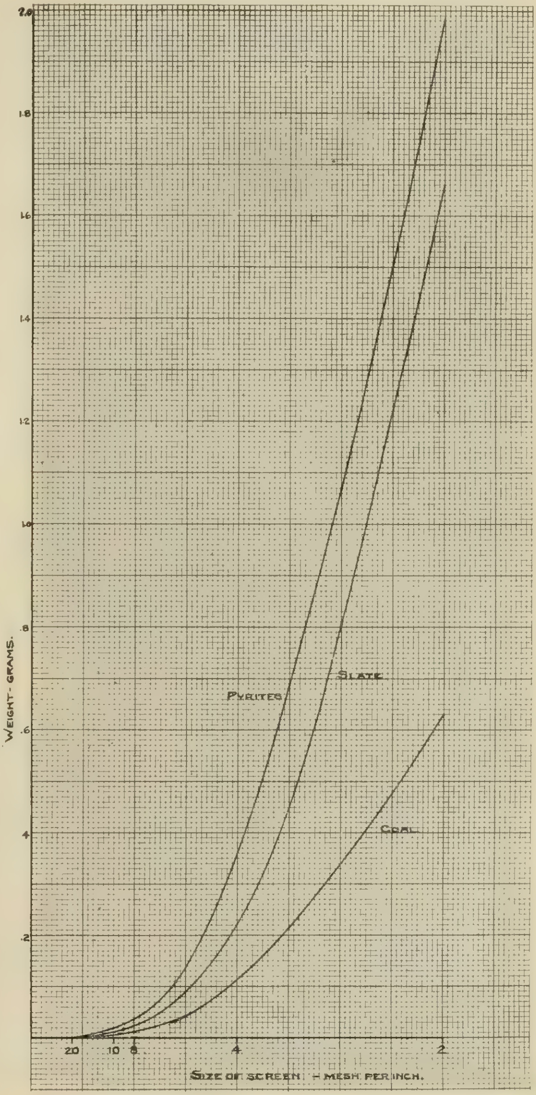


Fig. 9.

on the sample about to be divided, and the same piece would be double this percentage of one-half of the divided sample; so that in taking the original sample the largest piece need be only 0.02 per cent.

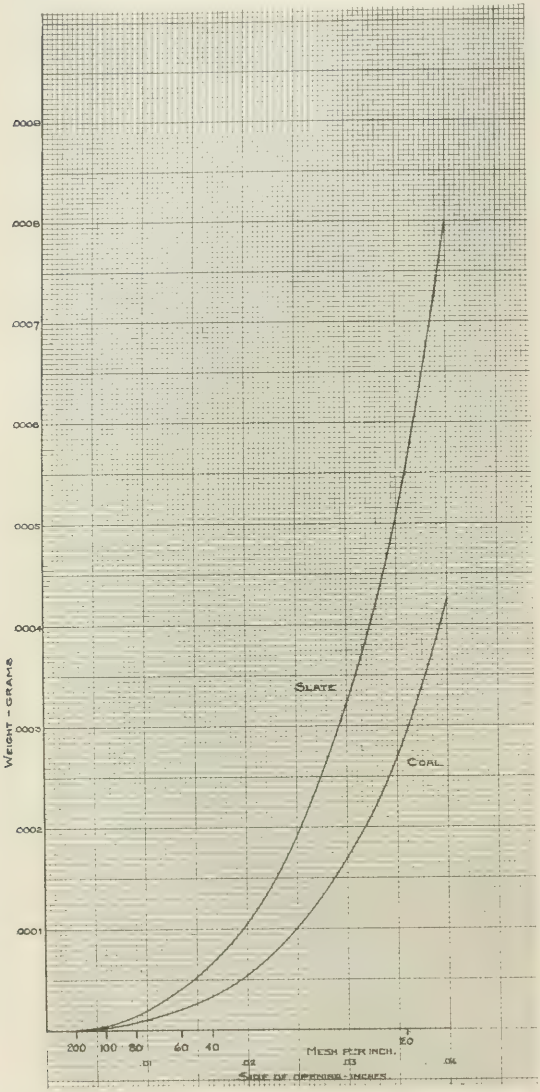


Fig. 10.

of the total and still be within the required limit of error.

TABLE V

(*a*) Size of slate contained in coal and amount of original sample required to insure the error of sampling being less than 1 per cent. ash.

Size of slate, inches.	Weight largest piece of slate Lbs.	Original sample should weigh. Lbs.
4	6.7	39,000
3	2.5	12,500
2	0.75	3,800
1½	0.38	1,900
1¼	0.24	1,200
1	0.12	600
¾	0.046	230
½	0.018	90

(*b*) Size to which slate and coal should be broken before quartering or dividing samples of various weights:

Weight of sample to be divided Lbs.	Should be broken to inches.
7500	2
3800	1½
1200	1
460	¾
180	½
40	2 mesh
5	4 "
½	8 "
¼	10 "

(*c*) Limit beyond which sample should not be divided when crushed to different sizes in laboratory:

Size of coal. Mesh.	Should not be divided to less than Gram.	
2	8300	
4	1100	
8	120	Should be pulverized to at least 60 mesh
10	55	
20	3	

Table V gives data which will be found very useful as a guide in sampling coal under various conditions. From this table, which is based on a "size-weight" percentage of 0.01 and coal containing 5 per cent. ash as slate and free impurities, the importance of taking a large initial sample will be realized. The size of the original sample is undoubtedly the weakest point in the existing methods of sampling coal, and the absurdity of a 100-pound sample is apparent. In collecting the original sample, the coal should be taken in fairly large increments. The taking of handfuls or small shovelfuls of run of mine or large-size coal makes it practically impossible to obtain a really representative sample in the beginning. Increments of 15 to 20 pounds are none too small in order that the lumps and fine may be proportionally represented. However, unless the importance of the "size-weight" percentage is realized by the chemist, a

sample—no matter how well taken from the original lot of coal—may be ruined by quartering to a smaller quantity than is proportional to the size to which it has been crushed.

The methods used by the average person in taking samples to be sent to commercial laboratories is sufficient explanation for the lack of confidence they have in the analysis as made by the chemist. While the complete history of the sample is seldom available to the chemist, yet he can determine the relation between the size and weight of the sample as it comes to him. From a large number of such samples received during the past year, there have been less than 3 per cent. of them where the largest pieces were 0.02 per cent. or less of the total. Table VI gives a classification of the condition of commercial samples as received from various sources.

TABLE VI.

"Size-weight" per cent. of sample as received.	Per cent of samples received from outside parties.
Less than 0.1	12
Between 0.1 and 0.5	13
" 0.5 " 1.0	20
" 1.0 " 2.0	24
" 2.0 " 3.0	13
" 3.0 " 4.0	3
" 4.0 " 13.6	15

Oftentimes some of the above samples have been half of a sample which has been divided between two laboratories, and when the results show a wide variation, as they naturally would, it is impossible to convince the person sending the samples that the fault is more likely to be in the dividing of the sample than in the analytical work. For his own protection, the chemist should determine the exact condition of any such sample when received at his laboratory and report same on the certificate with the analysis. This relieves him of much controversy and has been found to be a very effective method of showing the public the folly of paying \$5 to \$25 for the analysis of a 25-cent sample.

SUMMARY.

1. The present methods of sampling coal are almost as various as is the number of persons taking such samples, with the result that errors of 3 to 5 per cent. in ash are of ordinary occurrence and extreme errors of 15 to 30 per cent. are frequently encountered.

2. The method of taking a sample must be specified in every detail in contracts between the two parties buying and selling coal on an analysis and heat unit basis before satisfaction, and justice will be given to both parties.

3. The errors in sampling evidently follow the laws of chance when any one method is used, and from the calculated probable errors a comparison of the accuracy of different methods can be made. See Table I and Fig. 1.

4. The most important factor causing errors in sampling is the size and number of pieces of slate, pyrites, bone and other impurities in proportion to the weight of the sample when originally taken or when divided or quartered. This ratio has been termed the "size-weight" percentage, (and the results of 193 analyses from different samples of the same coal show that there is a decided increase in the percentage of error in ash with the larger "size-weight" percentage.) See Table II and Figs. 2 and 3. note 3.

5. From over 1300 divisions of samples containing marked pieces of coal it was found that the variation in the number of pieces in each half varied according to the law of probability, and that the variation increased with the number of pieces in the sample divided. From this data an empirical formula was deduced, which showed that the error in dividing a sample is a function of the percentage of ash due to slate, etc., and the "size-weight" percentage. The error calculated by means of this formula checked remarkably close with the results of actual analyses. See Table III and Figs. 4, 5 and 7.

6. The average of any number of samples reduces the error in proportion to the square root of the number averaged, providing all samples have the same "size-weight" percentage; or, if a certain degree of accuracy is required a less aggregate weight of original sample need be taken when two or more samples are obtained and averaged, see Fig. 6.

7. The weight of various sizes of slate and coal was determined by weighing up a large number of each, passing through a screen or sieve of one size and over the one of the next smaller size. The sizes ranged from 4 inches bar screen to an 80-mesh sieve. This data is given in Table IV and Figs. 8, 9 and 10.

8. A knowledge of the relation existing between the "size-weight" percentage, amount of ash due to slate and the possible error, makes it feasible to intelligently take a sample of any coal with an assurance that the results will be accurate within certain limits. See Table V, also Figs. 2, 3, 5 and 6.

9. The deductions from the experiments and data reported in this paper explain the cause of

many samples varying so widely in quality, even though taken from the same car or lot of coal, the most common fault being that the original samples taken have been too small. The absolute necessity of taking large samples will lead to mechanical or automatic sampling in many places.

10. The chances of error in the chemical analysis are insignificant when compared with the errors in the existing methods of sampling coal. The chemist should be responsible for the sampling in every possible instance.

11. Almost every one who has given any consideration to the sampling of coal or other similar material, has said that a large sample should be taken and that it should be broken or crushed fine before the successive quarterings. How large, and how fine, have been left to the judgment of the individual taking the sample, and it is the object of this paper to answer these questions with some degree of accuracy. As this data is of a preliminary nature, it is hoped that others will not only verify these results, but add to them, in order that the sampling of coal and other material may be reduced to a more scientific basis.

THE COMMERCIAL MANUFACTURE OF AMORPHOUS CALCIUM PHOSPHIDE.

By Charles E. Munroe.

Received January 8, 1909.

In 1891, I was directed to prepare calcium phosphide on a limited commercial scale. The Howell Automobile Torpedo had then been developed to such an extent that it had been tentatively accepted as a service weapon, and officers and seamen gunners of the Navy were being trained, by target practice, to become skilled in its use. As devised, this torpedo was so constructed that, as ready for service, it would, when stationary or running at low speed, fill with water to such an extent as to sink the torpedo and drown its priming charge and detonator so as to render them harmless, for, if in action a live torpedo failed to hit the enemy at which it was aimed and became vagrant, it would prove a menace to friend as well as foe. Although, in target practice, the war heads were not used it was necessary that otherwise the torpedo should be arranged and should operate as in action. But the sinking of the torpedoes at the end of their runs was, owing to the difficulty of locating them in deep water, a serious impediment to practice, as they were expensive. Hence, it was most desirable to recover them. Various devices were invented with the object of surmounting this difficulty. The one which proved most efficient was the inserting in the nose of the torpedo of a can of calcium phosphide, with holes punctured in the top of the can, for as the torpedo took the water the reaction of the phosphide with the water entering the can gave rise to a cloud of smoke, which was visible by day, and a faintly luminous flame, which was visible by night, and these phenomena enabled one not only to easily follow the course of the torpedo during its run but also to locate it with great accuracy after it had sunk. It thus became easily possible to recover the torpedo by grappling.

As there was, previous to the erection of this furnace, no manufacture, so far as was known, of calcium phosphide in this country, it was imported from Europe at a cost of $2.25 per pound. Quite apart from the high cost a difficulty was met in importing it, owing to the custom's officers, who insisted on breaking open the sealed packages and inspecting their contents greatly to the disgust of both the inspecting officers and the importers, though for different reasons, and to the damage of the material. For these various reasons, I was directed to manufacture it and the material was then supplied by the Government to the company furnishing the torpedoes.

From the literature it was learned that Dumas[1] placed fragments of quicklime in a retort set horizontally on a grate and disposed phosphorus at the extremity of the neck, which was closed with a stopper. When the lime had been heated to redness the phosphorus was passed over it in the state of a vapor, thus producing calcium phosphide.

Thenard[2] made use of a clay crucible, of about 1 liter capacity, pierced at the bottom by a hole 1 to 2 cm. in diameter. The neck of a glass flask, of about 250 cc. capacity was passed through the hole in the bottom of the crucible and luted in place, and the whole arranged in a furnace with a double grate so that the flask hung suspended above the lower grate. The flask was filled with phosphorus and the crucible above it with quicklime. When the lime had been heated to redness, heat was applied to the glass flask and thus the vapors of the phosphorus were passed through and about the lime. The operation lasted 30 to 40 minutes and about 500 to 600 grams of the phosphide were obtained.

[1] *Ann Chim Phys* [2] **33**, 363 (1826).
[2] *Ibid.* [4] **14**, 12 (1845).

A preferred form of crucible recommended by Thenard, was one which was divided into two parts by an earthenware grid, the lower section, about 1/3 to 1/4 the height of the crucible, being used to hold the phosphorus. Such a crucible is pictured by Pelouze et Fremy[1] but they effected the division by placing a small crucible inside the large one and placing the grid on the small one. However, they continued the use of a furnace with two grates.

Gattermann and Haussknect[2] made use of a covered Hessian crucible, resting on the grate of a crucible furnace, in which to put the lime, and when the latter had been brought to a glow, they dropped in sticks of phosphorus by means of a vertical iron tube which passed through the covers of the furnace and crucible, and reached to within 2 cm. of the bottom of the crucible, the upper end of the iron tube having a glass tube fitted into it by means of an asbestos packing.[3] They used about 500 grams of lime and added to it 350 to 400 grams of phosphorus.

This was the state of the art as I found it at the time of beginning this work. Experiments were made with glass and earthenware vessels, but they proved unsatisfactory. Tests were then made with an iron tube, butt-welded at one end, and this resisted the action of molten and vaporized phosphorus so well that crucibles were made from 5 inch wrought iron tubes with welded bottoms, their dimensions being as follows: depth inside 6 inches, outside 7 inches, diameter at top, inside 5 inches, outside 5 5/7 inches. They were provided with grooved lids, 1/4 inch thick and 6 inches outside diameter, which were fitted with asbestos gaskets. A slotted lug was welded on each side of each crucible and a wedge-shaped iron key was provided so that by driving it through the slots the cover of a crucible was easily fastened on tightly and firmly. Through one side of the cover a wrought iron pipe, 12 inches long, and 1 inch in diameter, was swedged, the lower end of the pipe being flush with the inside face of the crucible cover. This pipe was provided with a cap 4 inches long and 1 1/4 inches inside diameter. Three of these pots are shown in the photograph. They held about 1500 grams of lime each. They were heated with coal in an ordinary square crucible furnace.

[1] *Traite de chimie*. **2**, 558 (1865).

[2] *Berichte*, page 1175 (1890).

[3] This apparatus, except for the glass extension tube, is practically identical with that of M. Silas shown in Mémoires Militaires et Scientifique, **5** [XXXII], pp. 9, 1877.

The lime used was "black marble lime, wood-burned." It was of high quality and it was broken into lumps 1 to 1 1/2 inches in diameter. The crucible was charged with the lime, the cover put on and keyed, and the whole lifted by the feed pipe and embedded in the fire in the furnace. When the crucible had become heated to between a dark and cherry redness the cap was lifted from the feed pipe, sticks of dry phosphorus were dropped in and the cap replaced. So soon as fuming ceased, which with the right proportion of phosphorus was almost immediately, the crucible was lifted from the furnace and allowed to cool with the cap on so as to prevent air from reaching the phosphide in any considerable volume during the cooling process. The operation required about 1/2 hour. With 1400 grams of lime to the pot and 200 grams of phosphorus added about 1600 grams of phosphide were obtained. With a larger quantity of phosphorus the yield was no greater as the excess of phosphorus fumed off. Using four pots, an unskilled workman, after short practice, turned out 28 pounds per short day. The cost, counting labor and materials, was 20 cents per pound. The same pots were used, without repairs, for some eight years.

The phosphide produced in this way was very active, giving off spontaneously inflammable hydrogen phosphide promptly on contact with water. A perforated tin container holding a pound of this amorphous calcium phosphide, when submerged in 18 feet of sea water, gave a flame, which rose some two feet above the surface of the water, and voluminous smoke, and it continued intermittently to give off flame and smoke for over five hours. It was found to be more satisfactory in its behavior than the imported article. Portions of it made 17 years ago seem to-day to be as active as when freshly manufactured.

Since this work was accomplished, H. Moissan[1] has obtained calcium phosphide by reducing tricalcium phosphate with carbon in an electric furnace, and also by the action of phosphorus on metallic calcium. The product thus obtained was crystalline and it reacted with water to produce phosphine (H_3P), which was not spontaneously inflammable, while the product obtained by the action of phosphorus on lime, after the manner described above, is amorphous and reacts with water to produce hydraphosphine (H_4P_2), to which is attributed its property of generating a spon-

[1] *Comptes rendus*, **128**, 787 (1898).

taneously inflammable product. E. Renault[1] has also obtained the crystalline calcium phosphide in the electric furnace, carrying out the operation in both iron and carbon crucibles, but he states that under certain circumstances he obtained, from the tricalcium phosphate, a phosphide which yielded both H_3P and H_4P_2. This is quite to be expected for I recall that when operating the plant at Spray, N. C., in 1895, for the production of calcium carbide I noted the presence of calcium phosphide in the product, due to reduction of calcium phosphate in the lime, and I attributed the spontaneous inflammation of the acetylene, and other gases, produced by the reaction of the carbide with water, to the simultaneous formation of hydraphosphine.

No doubt if there were any considerable demand for amorphous calcium phosphide it could be most economically met by electric furnace methods, but as the uses for this material are limited the method I have described is sufficient and commends itself for its simplicity, low cost of installation, the wide accessibility of the apparatus and materials used, and the ease with which it can be carried out by unskilled labor.

With this manufacture in successful operation in the Navy there was naturally a desire to further utilize the product in the solution of other naval problems. It had then been recognized that the electric search lights installed in the Navy were not an unmixed blessing for while they might be used in locating the enemy they never failed also when in use to locate the vessel that carried them, and therefore they failed in enabling one to take the enemy by surprise. It was evident that this defect could be remedied by means of a self-igniting light which could be thrown, say in a shell from a gun, among the enemy. With this in view, experiments were made with the product from this furnace but though perfectly clear, yet quite dark, nights were chosen for the tests, when the vessels in the harbor were at anchor with some of their sails spread, and the seamen

[1] *Comptes rendus*, **128**, 883–884 (1898).

gunners who laid the test shells were clad in white duck working suits, yet the intrinsic luminosity of the phosphide flame was so slight that no useful result was obtained. Quite recently, however, according to reports, this result has been successfully accomplished and we find in calcium carbide, mixed with calcium phosphide, a material which, when thrown to a distance, will, when alighting in water, produce a self-igniting flame which has a high intrinsic illuminating power.

But the economic use to which this material has been longest put and even to-day, probably, the chief use to which it is put, is as an attachment to life-saving emergency buoys which are carried aboard passenger vessels in locations from which they may be readily thrown at the call of "Man Overboard," for though the flame given by the phosphide is dim yet it is often sufficient to enable the person struggling in the water to locate the buoy. This application is described in great detail in De l'application de phosphure de calcium a l'appareil éclairant des bouées de sauvetage,[1] and it therefore will not be enlarged upon here.

THE GEORGE WASHINGTON UNIVERSITY.

THE TEMPERATURE OF THE LEAD BUTTON IN CUPELLATION.

BY ROBERT H. BRADFORD, PH D., Prof of Metallurgy, State School of Mines, University of Utah.

Received December 24, 1908.

Excellent work with the assay furnace was done by early investigators. They had no means of ascertaining exact temperatures, and hence in their writings they attempt to describe the desired temperatures by the appearance of the objects to the eye, using such color terms as would most nearly apply to the degree of heat under consideration. They recognized the importance of employing proper muffle temperatures in cupellation, as is indicated by the following careful description of the same given by an early text-book on assaying:[2] "When the interior of the muffle is reddish white the matters to be cupelled may be introduced. When the cupels are filled, the furnace is closed, either by the door or by pieces of lighted fuel, so that the fused metals may become of the same temperature as the muffle. When this point has been gained, air is allowed to pass into the furnace; the metallic bath is then in the state termed 'uncovered;' that is, it presents a convex surface, very smooth, and without slag. When the air comes in contact with it, it becomes very lustrous, and is covered with luminous and iridescent patches, which move on the surface, and are thrown toward the sides. These spots are occasioned by the fused oxide of lead which is continually forming, and which, covering the bath with a very thin coating of variable thickness, presents the phenomenon of colored rings.

"As silver is sensibly volatile, it is essential, in order that the smallest possible quantity be lost, to make the cupellation at as low a temperature as may be. On the other hand, the heat ought to be sufficiently great, so that the litharge may be well fused and absorbed by the cupel.

"Experience has proved that the heat is too great when the cupels are whitish, and the metallic matter they contain can scarcely be seen, and when the fume is scarcely visible and rises rapidly to the arch of the muffle. On the contrary, the heat is not strong enough when the smoke is thick and heavy, falling in the muffle, and when the litharge can be seen not liquid enough to be absorbed, forming lumps and scales about the assay. When the degree of heat is suitable the cupel is red, and the fused metal very luminous and clear."

Modern texts are less elaborate in their descriptions, yet they lay especial stress on the importance of maintaining proper temperatures in the assay muffle.

The modern pyrometer, for accurately measuring high temperatures, has recently come to fill a long-felt want in many metallurgical operations. Since the need of employing definite temperatures in assaying is generally recognized, one would expect that the pyrometer would be employed more commonly in the muffle, and greater accuracy observed in stating degrees of temperature. It is gratifying to see some recent magazine articles and texts on assaying employing exact figures for representing temperatures required for the various operations in the furnace.

It is difficult to reconcile some explanations of cupellation phenomena, based on pyrometer readings, with certain well established facts. The lack of sufficient exact data may account for some apparent discrepancies, as the following instance will show. One very recent manual of assaying[1] in describing the process of cupellation says: "Little flakes of PbO form on the surface of the

[1] Mémoires Militaires et Scientifiques, 1878, XXXII.

[2] John Mitchell: "Manual of Practical Assaying," 2nd edition, p. 368–370 (1868).

[1] C. H. Fulton: "Manual of Fire Assaying," 1907, pages 70, 71.

molten lead and slide down the convex surface of the button, and are absorbed by the porous mass of the cupel. If the temperature of the cupellation is between 700 and 750° C. as it should be, this litharge is solid, as litharge melts at 906° C." The same author says further that the actual temperature of cupellation has never been determined, and that a determination of the temperature of the cupelling lead will, in his opinion, very much modify the present theory.

If it is necessary as stated by Mitchell to have the driving lead button constantly hot enough to keep the litharge in a molten condition, in order that the oxide shall be absorbed by the cupel, then the temperature of 700 to 750° C. as used by Fulton cannot be high enough, if applied to the button, because litharge freezes at 906° C.

It was with the object in view of determining the minimum temperature of a cupelling button, that the series of experiments herein reported were undertaken. The instrument used in the experiments was the Le Chatelier thermo-electric pyrometer, illustrated in Fig. 1. It consists of a platinum wire and a 90% platinum 10% rhodium wire twisted or soldered together, forming a thermo-electric couple, the loose ends of the wires being attached by means of copper leads to a galvanometer of high resistance. The cool ends of the wires were kept at a known temperature by being immersed in water along with a thermometer. The twisted junction of the wires was readily placed in any position in the muffle. In order to calibrate the instrument the deflections and cold junction temperatures were taken with the twisted junction at certain known temperatures. A curve was then plotted, showing the relationship between deflection and temperature. From such a curve any deflection of the galvanometer was interpreted in degrees Centigrade.

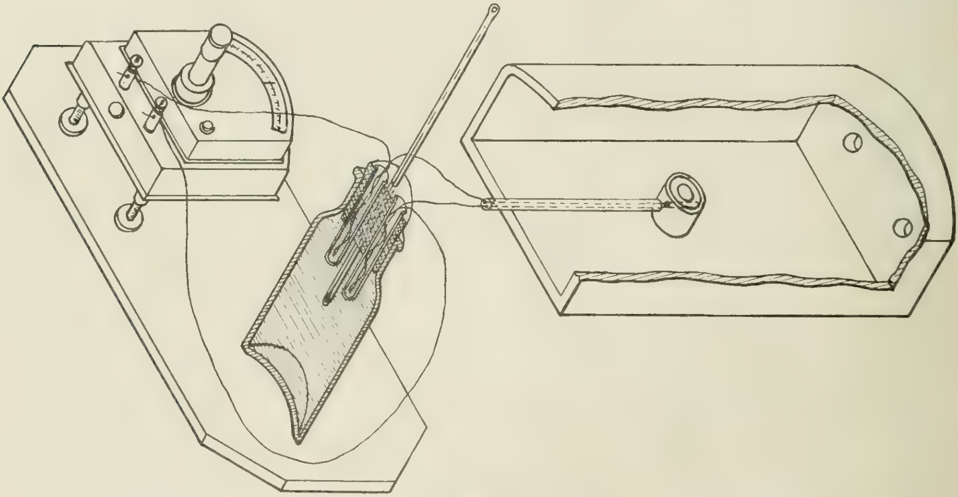


Fig. 1.

Since it is necessary to have a draught of air through the muffle in order that oxygen may be supplied to the cupelling button and since the air is cool as it enters the muffle, the temperature of the air above the button is considerably lower than that of the muffle itself or of the cupel interior, and very much lower than that of the cupelling metal. In previous magazine articles and text-book descriptions the recorded temperatures are apparently those of the surrounding atmosphere rather than the lead button, and very little information is on record concerning the temperature of the driving button.

When the bare pyrometer wires were brought in direct contact with the driving lead they were immediately alloyed and fused. To prevent this destruction of the wires when employed with molten lead the couple was protected at the hot junction by a thin coating (see Fig. 2) of fire-clay. This coating was made on the spot from moistened raw material. It was made thin so that it would offer but little interference with the surface oxidation of the lead button. The temperature of the heat-

ing button was determined by placing the protected couple well within the molten lead, then reading the galvanometer and the cold junction thermometer, and interpolating on the calibration curve to find the degrees Centigrade.

The minimum temperature of the lead button itself requisite for starting cupellation was investigated by introducing buttons into cupels placed at varying distances from the front of the muffle and hence at varying temperatures. Pyrometer readings of the heating metal and the cupel interior were carefully taken in each instance.

Before driving commenced it was found that the temperature of the molten metal rose to 900° C. or above—approximately to that of melting litharge. If the heat conducted from the cupel or radiated from the muffle was not sufficient to raise the temperature to that of melting litharge the button froze and would not "uncover."

In order to confirm the temperature readings of the cupelling metal the degree of heat of the interior of the cupel was determined by boring a small hole into the dry cupel with a one-eighth inch drill bit, and inserting the junction of the pyrometer wires well within the cupel. Holes were drilled to points beyond the centers of the cupels, and were made at different levels in the different cupels, from directly underneath the bottom of the cup-shaped depression, to the bottom of the cupel directly above the supporting muffle. The method of getting the temperature of the cupel interior is illustrated in Fig. 2.

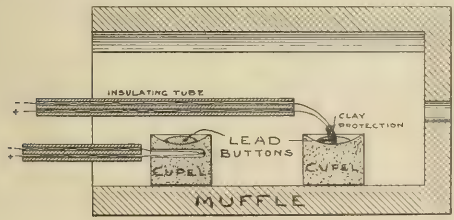


Fig. 2.

The temperature of the interior of the cupel was readily ascertained by the method previously described. In every case in which the cupel had been properly pre-heated beforehand, as is done in ordinary practice, the temperature directly under the button, although lowering as the lead melted, rose to 900° C. or above before cupellation commenced. Below this point and nearer the muffle the temperature was usually a few degrees higher when the button opened. The melting metal had taken its heat from the upper layers, cooling these more than those near the bottom.

The temperature within the cupel and near the molten lead remained at 906° C. or above so long as the button continued to drive. If the button froze the temperature of the interior rapidly lowered, showing that its heat had been, in great part, derived from the heat of combustion of the driving lead. Upon freezing, the temperature of the button rapidly declined because its heat of combustion had been cut off.

If the interior of the cupel was well below 906° C. when the button was introduced and the cupel and contents then pushed back into the muffle, the button began to drive when the heat radiated from the arched roof of the muffle gave the litharge coating of the lead a temperature of 906° C. The bare couple could be safely placed in contact with the litharge in the above instance. The button rapidly heated to a much higher temperature if left in this position as cupellation proceeded. An intensity of heat resulting from the above conditions is not safe to use, owing to the excessive losses in silver and gold. Good practice would require that the cupel and contents be drawn forward to a cooler part of the muffle.

The temperature favorable for the formation and retention of "feathers" of litharge was determined by placing the bare couple among the crystals as they formed around the button. The temperature of the forming crystals in every instance was below 906° C. as measured near the driving lead. So long as the button continued to drive, the cooler the surrounding air and cupel surface, the more favorable was the temperature for the formation of the litharge crystals. After the cupellation was finished these crystals could be heated to 850 to 890° C. for many minutes without showing any tendency to fuse as indicated by their sharp edges, and without volatilizing to any considerable extent. If their temperature was raised to the melting point of litharge they immediately fused and were absorbed by the bone ash cupel.

The results of these experiments seem to establish the following facts:

When once the lead commences to oxidize rapidly and the molten litharge escapes into the cupel, the temperature of the button immediately rises owing to the heat of combustion of the oxidizing lead, and the heat from this source is sufficient

to keep the button driving, *i. e.*, to keep the litharge molten and thus in a condition to run down the sides of the button and in most part to be absorbed by the cupel—even though the cupel and contents are drawn forward to a cooler position. With a gentle draught through the muffle the temperature one-quarter inch above and near the front of the cupel may be maintained as stated by one text,[1] as low as 625–650° C. and cupellation continued, although the danger of freezing is very much lessened if the temperature is kept between 650° and 750°. So long as the heat of combustion of the driving button is able to maintain the temperature of the lead at that of melting litharge the cupellation proceeds. If the cupel is brought so near the mouth of the muffle that the transference of heat from the button is sufficiently rapid to overcome the heating effect of the combustion of the lead, the button cools; and when its temperature goes below the freezing point of molten litharge, it freezes, *i. e.*, solid litharge covers the molten lead and cupellation ceases.

If the surrounding air is kept well below the temperature of melting litharge, the surface of the cupel around the driving button becomes cooled below that temperature, and the molten lead oxide as it runs off the convex surface of the lead, solidifies, and crystals of litharge, or "feathers" form. These thin crystals volatilize slowly after forming, but do not disappear as a rule unless the temperature of the cupel surface is raised above 906° C. when they melt and are partly absorbed by the bone ash of the cupel.

UNIVERSITY OF UTAH,
SALT LAKE CITY.

[1] Richard W. Lodge: "Notes on Assaying" (1905), page 60.

A NICKEL CRUCIBLE FOR THE DETERMINATION OF CARBON IN STEEL.

BY HENRY E. K. RUPPEL.

Received November 27, 1908.

The high price of platinum crucibles for carbon determinations led the writer to seek some substitute to supplement the work of the Shimer crucible in regular use in his laboratory. Nickel naturally suggested itself for this purpose on account of its inexpensiveness, its high melting point and its resistance to oxidation. Crucibles of this material have been used for the past year for the determination of carbon in steel and the results, obtained both by direct combustion of the steel and by solution in potassium copper chloride, have been so satisfactory that it seemed advisable to publish them together with a description of the apparatus.

At the beginning, a word should be said in regard to the conditions under which such crucibles can be used to advantage. A conservative estimate of the life of these crucibles is about thirty to fifty determinations when the solution method is used. On account of the low cost of these crucibles they can be used to advantage in those analytical laboratories where the number of carbon determinations performed is limited and the high initial cost of platinum precludes its use, especially in college laboratories where a single crucible may serve the needs of an entire class. They may also find a place as supplementary crucibles in steel laboratories where carbon determinations are a matter of daily routine. Since such crucibles are used up in time, it is necessary to make them as simple as possible and to provide for a separate water jacket not directly attached to the crucible.

The principle of a water-cooled stopper for platinum crucibles to be used in the determination of carbon in steel was first published by P. W. Shimer[1] and several forms are at present on the market. Although the present paper is intended solely to show that satisfactory results can be obtained with a nickel crucible, nevertheless the writer feels justified in giving a somewhat detailed description of the cooling apparatus as the design is particularly adapted to the simple form of nickel crucible employed.

The apparatus is shown in Fig. 1 and 2. Fig. 1 is a top view and Fig. 2 is a vertical section through the dotted line $x\ y$. It consists of three parts; the nickel crucible A, the cover C and the water jacket B. The nickel crucible is 1 7/8 inches deep, 1 9/16 inches in diameter at the mouth and is provided with a flange about 9/16 inch wide. These crucibles are now supplied to us in one piece, although we have used ordinary nickel crucibles to which a brass rim was soldered with silver solder. The area of the bottom was made comparatively large so that all the carbon might be in contact with the bottom of the crucible, even though the asbestos pad was made slightly large as sometimes happens. When this occurs with the platinum crucible, in which the

[1] "Carbon Combustion in a Platinum Crucible," *J. Am. Chem. Soc.*, **21**, 7 (1899).

area of the bottom is small, the asbestos pad as well as the asbestos used to wipe out the funnel, extends up the sides of the crucible. In such cases we have sometimes encountered unburnt carbon. This difficulty is further obviated by using a deep crucible which can be heated to a considerable distance from the bottom. It might be stated against this that an asbestos pad made in an ordinary funnel is not too large to fit comfortably in the bottom of the regular platinum crucible. On the other hand, the filtration becomes slower as the area of the pad decreases. We use a special funnel which will be described later and which offers a comparatively large area for filtration.

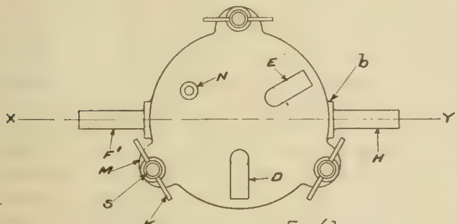


Fig. 1.

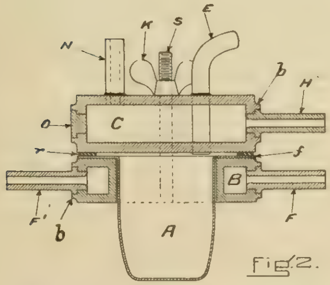


Fig. 2.

The crucible rests upon the water jacket *B*, which consists of an annular machined bronze casting 2 3/4 inches outside diameter, 1 9/16 inches inside diameter and 5/8 inch high with walls about 1/8 inch thick. This jacket is provided with two 3/8 inch holes, each of which is surrounded by a boss *b*. The holes are slightly counter-bored and the collars of the brass tubes *F* and *F'* are inserted and fastened with ordinary solder. The brass tubes are all turned from solid stock and are 1/4 inch outside diameter with 1/8 inch holes. Three brass rods *S*, 3/16 inch in diameter and threaded at each end, are permanently soldered to the ears, corresponding to *M* (Fig. 1) with which the jacket is provided, and pass through holes in the corresponding parts of the cover which is keyed down by means of the winged nuts *K*.

The cover *C* is also cast of bronze and machined. It is 2 3/4 inches in diameter, 7/8 inch high with walls about 1/8 inch thick. It is supplied with three semi-circular ears M, 3/4 inch in diameter, through which holes are drilled to admit the rods *S*. In making these castings it was necessary to provide two 3/8 inch holes through which the anchors of the core might be passed. One of these holes is closed by the brass plug *O* (Fig. 2), the other is counter-bored and the collar of the brass tube *H* inserted and soldered. The joint between the crucible and the cover is made tight by means of a rubber gasket *r* such as is used for ordinary glass preserve jars. The air enters the crucible by tube *D* (Fig. 1), which extends 1 1/4 inches below the cover, and leaves by the tube *E*. The top ends of these tubes were bent in an ordinary blast lamp after filling them with sand. When in use tubes *F* and *H* are connected by means of a rubber tube. The water, supplied by an eighth-inch tap, enters the jacket at *F'* and leaves the cover through the tube *N*.

The cost of the nickel crucible is one dollar and ten cents. The cost of the completed jacket and cover, exclusive of patterns, is about seven dollars.

The determinations given in Table I were made by dissolving the steel in double potassium copper chloride solution, filtering on ignited asbestos, and burning in a current of air. The crucible was supported through a hole in a piece of asbestos board 1/4 inch in thickness and was heated to bright redness for 3/8 to 1/2 inch from the bottom by mean of a small upright blast lamp. The time of heating was half an hour for steel and three-quarters of an hour for cast iron. Instead of using an ordinary funnel for filtering the carbon, we employed a modified form of the funnel generally used to support a Gooch crucible, in which the height of the funnel above the stem is about one inch. A copper wire is made into a close spiral at one end and passed through the stem of the funnel, loose asbestos is added, followed by a suspension of asbestos in water. After applying the suction, the asbestos is gently tamped down with the flattened end of a glass stirring

rod. The finished pad is from 3/4 to one inch in diameter and about 1/4 inch thick. This pad is placed in the crucible with the carbon down and the crucible is filled loosely with ignited asbestos. The bottom is protected by means of sheet platinum shaped so as to fit snugly inside and to extend about 1/4 inch up the sides.

The combustion train consists of a small preheating furnace containing a twelve inch porcelain tube filled with copper oxide, followed by a Liebig bulb containing potassium hydroxide solution and a small guard tube. Next in order comes the crucible, a small furnace with a twelve-inch porcelain tube containing copper oxide, a tube of beads moistened with water, a Marchand drying tube and the Geissler bulb and guard tube. The writer prefers the small porcelain tubes to the brass tubes frequently used and employs them with the platinum crucible. The above procedure is the one regularly used on carbon steels in his laboratory.

In Table I, column 1, are given some of the results obtained with the nickel crucible, column 2 contains the corresponding results obtained with the platinum crucible, except in the case of cast iron, in which the results given in column 2 are the average of the results of various chemists on standard foundry iron. The results are representative and were not selected on account of their agreement. Blanks can be easily obtained showing an increase in weight of less than 0.5 milligram and the results agree closely with those obtained by means of the platinum crucible. Many of the samples were mixtures from several rolls so that some of the variations may be due to imperfect mixing.

TABLE I.

Sample.	1. Nickel crucible. Per cent.	2. Platinum crucible. Per cent.
1	1.119	1.114
2	1.082	1.081
3	1.185	1.187
4	1.132	1.115
5	1.023	1.022
6	1.090	0.070
7	1.118	1.098
8	1.127	1.141
9	1.074	1.077
10	1.108	1.084
11	1.052	1.053
12	1.133	1.132
13	1.086	1.087
14	0.936	0.936
15	1.163	1.163
16 Cast iron A	3.63	3.67
17 Cast iron D	3.01	3.00

	Mg.
Blanks (15 minutes)................	+0.3
" "	0.0
" "	+0.1
" "	+0.0
" (30 minutes)................	+0.4
" "	+0.6
" "	+0.3

In Table II, column 1, are given the results obtained by direct combustion of steel in a current of oxygen. In column 2 are given the corresponding results found by dissolving the steel in potassium copper chloride and burning the carbon in air.

To prevent the caked iron oxide from adhering to the platinum shell, which protects the bottom of the crucible, it is filled to a depth of about 1/16 to 1/8 inch with ignited aluminum oxide, which is tamped down in the middle with the flattened end of a glass rod. Three grams of steel are carefully placed on the aluminum oxide so as not to touch the sides of the platinum. After filling the crucible with loose asbestos the steel is burned for thirty minutes in a current of oxygen. Air is then passed through the apparatus for at least thirty minutes to remove the oxygen. The samples used for the direct combustion of steel consisted of pieces about 1/16 inch square and about 0.006 inch thick. The iron oxide is readily removed at the end of the determination by withdrawing the platinum shell from the crucible. To prevent the platinum from adhering to the crucible it is advisable to remove it occasionally, especially while the crucible is new.

TABLE II.

Sample.	1. Direct combustion. Per cent.	2. Solution method. Per cent.
1	1.123	1.137
2	1.151	1.144
3	1.144	1.133
4	1.176	1.163
5	1.153	1.163
6	1.109	1.114
7	0.841	0.834
8	1.261	1.276

The following figures give some of the blanks obtained by passing oxygen through the apparatus for thirty minutes and expelling the oxygen by forcing air through for the same time:

+0.9 mg., +0.8 mg., +1.1 mg., +0.7 mg., +0.4 mg., +0.3 mg.

When the direct combustions in oxygen were first tried, the air was allowed to pass through the combustion train for only fifteen minutes to expel the oxygen, but the results obtained in this way were always too high. That this was mainly due to the presence of oxygen in the Geissler bulb is shown by the following experiments. After

attaching the weighed Geissler bulb to the train, oxygen was passed through at the rate of three bubbles per second for thirty minutes, followed by air at the same rate for fifteen minutes. The Geissler bulb was then detached and weighed, after standing in the balance case for fifteen minutes. The increase in weight was 7.4 mg. in one experiment and 5.2 mg. in another. While the bulb was in the balance case, air was passed through the rest of the train in order to remove any oxygen which might have been present. The Geissler bulb was again attached and air allowed to bubble through for fifteen minutes more. After allowing the bulb to remain in the balance case for the usual time, its weight was found to be practically the same as at the beginning of the experiment. This would seem to indicate clearly that the oxygen is not completely removed by passing air through the apparatus for fifteen minutes.

Many chemists do not expel the oxygen in this way but prefer to weigh the bulb containing oxygen instead of air; this would, of course, shorten the time considerably.

In conclusion, the writer desires to express his sincerest thanks to Professor Henry Fay for his interest and to his assistant, Miss Caroline E. Shute, by whom many of the determinations were made.

BOSTON, MASS.

DETERMINATION OF IRON IN BRASSES AND BRONZES.

BY I. M. BREGOWSKY AND L. W. SPRING.

Received January 15, 1909.

At various times we have had occasion to compare our analyses of brasses and bronzes with those of other chemists, on the same samples. It has practically always been noticeable that while the other chemists check us within fairly close limits on tin, lead, copper and zinc—the main constituents of brass, they nearly always either fail to mention the iron content, or report it as "a trace" or give some such value as 0.06 per cent., or possibly 0.20 per cent.—seldom more. With samples on which our determinations of iron have shown the iron content to be far above "a trace" in any sense of the term, the chemist of a well-known railroad made no mention of iron in his report, and a prominent commercial chemist reported "a little iron present" on one of the two samples, and did not mention iron in the report on the other. With another sample on which we got 0.75 per cent. iron, a metal refiner offered to wager us a snug sum that there was not over 0.006 per cent. of iron present. His chemist had reported a content of 0.003 per cent.

Now iron in the amounts present in the commercial copper alloys may or may not be considered to be a factor of importance in the usefulness or working of the alloy, yet the chemist should know what the iron content is, or at least know how to determine it when he wants it. There is little that is new in the method and many will say that such accuracy is unnecessary. However, when occasion requires some may profit by a knowledge of it.

Fresenius' "Quantitative Analysis," Cohn edition, 1904, p. 681, says that the stannic oxide obtained upon the ignition of the metastannic acid precipitate is impure, containing part of the iron, besides other impurities, and gives directions for separation. We have found, as a rule, approximately half of the iron content of the brass in the ignited stannic oxide, unless the iron in the alloy is high. The remainder will be found by precipitation with ammonia either before or after the copper is separated, if sufficient time be allowed for it to come down. Our procedure is as follows:

A gram of the magnetted borings is dissolved and run down in nitric acid (1.42), the metastannic acid filtered out as usual and ignited to stannic oxide in a clean weighed porcelain crucible. After weighing the stannic oxide, one gram of c. p. sodium carbonate and 0.25 gram of sublimed flowers of sulphur are added, the crucible covered and the mixture fused at a very low heat until the excess of sulphur is burned off. Crucible and cover, when cold, are immersed in 50 cc. of distilled water in a No. 1 beaker and warmed to disintegration of the melt. They are then rinsed and removed. If the solution is blue or green, it indicates dissolved iron which can be thrown out by addition of a little ammonium chloride, leaving the solution a light yellow. The ferrous sulphide is filtered out, rinsed with hydrogen sulphide water, dissolved from the filter, and the iron determined by titration or gravimetrically. The iron figured to ferric oxide should, of course, be deducted from the weight of the stannic oxide.

The lead and copper are removed and determined by any of the usual methods. The filtrate is brought to a boil, the iron oxidized with

a few drops of nitric acid and an excess of ammonia added. The solution is kept just at the boiling point for an hour or so. A bubble going up occasionally does no harm, but hard boiling does not allow the iron hydroxide to settle and undoubtedly has led many to believe that none was present. In an hour, the bottom of the beaker will show a considerable precipitate of iron hydroxide. It is filtered out, washed well with hot water, and determined volumetrically or gravimetrically. Blanks should be run on all chemicals used and their iron content allowed for.

We often analyze magnetted drillings from brasses from many sources and seldom find one with an iron content of less than 0.40 per cent., and many run to 0.90 per cent. and above. Below are given some of our analyses showing the total iron found and the relative amounts found in the stannic oxide and the main solution. Many of these samples have been analyzed by other chemists who, in their original analyses, found little or no iron, but who now by this method check the results here given.

BRASSES AND BRONZES (FINISHED GOODS) OF VARIOUS MANUFACTURERS.

	Sample No.						
	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.	5. Per cent.	6. Per cent.	7. Per cent.
Iron from SnO_2	0.30	0 25	0 34	0 32	0 16	0 63	0.16
Iron from main solution	0.63	0 26	0 43	0 28	0 20	0 84	0 25
Total iron..........	0.93	0.51	0 77	0 60	0 36	1 47	0.41

	Sample No.					
	8. Per cent.	9. Per cent	10. Per cent.	11. Per cent	12. Per cent.	13. Per cent.
Iron from SnO_2......	0.35	0.18	0 57	0.04	0.12	0.31
Iron from main solution..............	0.49	0 49	0.43	0 36	0.22	1.01
Total iron.........	0.84	0.67	1.00.	0.40	0.34	1.32

Nos. 6 and 13 were not manganese bronzes but ordinary brasses.

Brass ingots we have received from refiners gave:

	Sample No.					
	14. Per cent.	15. Per cent.	16. Per cent.	17. Per cent.	18. Per cent.	19. Per cent.
Iron from SnO_2......	0.39	0 37	0.24	0.24	0.22	0.33
Iron from main solution..............	0 34	0.33	0.28	0.98	0.49	0.32
Total iron...........	0.73	0.70	0.52	1.22	0.71	0.65

Samples of brass borings received from metal dealers, after removal of the free iron by magnet, gave:

	Sample No.				
	20 Per cent.	21. Per cent.	22 Per cent.	23. Per cent.	24. Per cent.
Iron from SnO_2	0 20	0 28	0 21	0 28	0 29
Iron from main solution .	0 35	0 35	0 63	0 43	0 32
Total iron..................	0 55	0 63	0.84	0.71	0.61

These results are sufficient to show that the ordinary copper alloy contains considerably more than "a trace" of iron. How necessary it is in a technical analysis to determine this iron is, of course, for the individual chemist or metallurgist to say. They also show that the quantity of iron carried down by the tin is, in the main, proportional to the amount of tin in the alloy.

	Sample above No.						
	11.	12.	13.	8.	2.	10.	6.
Per cent. of tin in the alloy................	1.13	2.28	3.34	8.20	6.04	5.97	5.67
Per cent. of iron in SnO_2	0.04	0.12	0.31	0.35	0.25	0.57	0.63

Undoubtedly the varying gelatinous condition of metastannic acid also influences the quantity of iron which is carried down.

CRANE CO. LABORATORY,
CHICAGO, January, 1909.

(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.)

THE COLORIMETRIC DETERMINATION OF NITRATES IN SOIL SOLUTIONS CONTAINING ORGANIC MATTER.

BY W. A. SYME.

Received December 9, 1908.

The accurate determination of nitrates in soil solutions by the colorimetric method with phenoldisulphonic acid and ammonia is a matter of some difficulty on account of the large number of interfering substances which may be present in the solution. Chlorides may cause a loss of nitric acid when the phenoldisulphonic acid is added to the residue left on evaporation. Iron salts affect the color. Nitrites interfere by producing a yellow color with the reagents like that caused by nitrates. These disturbing factors can be removed to a considerable extent—the chlorides by adding silver sulphate, the iron salts with sodium carbonate, and the nitrites may be determined separately by the Griess method.

The presence of organic matter in the soil extract causes trouble in several ways. In the first place, the solution may be so intensely colored that it cannot readily be decolorized with carbon black; secondly, the organic matter may reduce

the nitrates, thereby causing a loss of nitric acid; and thirdly, the strong acid acting on the organic matter produces substances of foreign color which cannot be matched by the pure nitrate standards.

The object of the work reported in this paper was to see if potassium permanganate could be used to remove organic matter from soil extracts. The extracts were prepared for some work on nitrification now in progress in this laboratory, the method of preparation being as follows: 400 grams of soil were shaken four hours with 1200 cc. of water containing a little chloroform. The solutions were filtered through a porcelain tube.[1] The filtrates were strongly colored when the soils contained much organic matter. The solution from soil 1867, a soil from a compost heap and the one most favorable for the nitrification experiments, was very rich in organic matter and could not be satisfactorily clarified by shaking with carbon black. When this solution was evaporated to dryness, the residue treated with phenoldisulphonic acid and made alkaline with ammonia, the resulting solution had a brownish yellow color quite different from the clear lemon-yellow given by a pure nitrate solution.

The method for treating this solution, and others of the same kind, was as follows: Heat 50 cc. or any convenient portion to 60–70° and add 1 cc. of dilute sulphuric acid (1 : 5). Add from a burette a dilute solution of potassium permanganate (5 to 10 g. per liter) until in excess and heat fifteen minutes on a water-bath, adding more permanganate from time to time, if necessary, to have an excess. Remove the brown precipitate by filtering into an evaporating dish, make the filtrate slightly alkaline with sodium carbonate and evaporate to dryness on the water-bath. Add water to the residue and filter into a 50 cc. flask, wash the residue on the filter, and dilute to the mark. We now have 50 cc. of a colorless soil solution nearly free from organic matter. Nitrates can now be determined by the usual colorimetric method, remembering that if nitrite were present in the original solution, it would be oxidized to nitrate.

If a soil solution, after treatment in the way described, is evaporated and the color, developed in the usual way, is compared with that given by a portion of the same solution not so treated, the difference is very marked.

[1] Bulletin 31, Bureau of Soils, p. 12.

The evaporation of the soil solution with sodium carbonate removes manganese and iron, but enough nitrous acid may be taken up from the air to give an appreciable color with the nitrite reagent.

Carbonaceous matter was not entirely removed by the treatment with permanganate, though the coloring matter was destroyed and the residue left on evaporating the solution to dryness on the water-bath was colorless. The quantity of carbonaceous matter left by the permanganate was not enough to cause a serious trouble when the phenoldisulphonic acid was added. The effect of the permanganate treatment can be readily seen by evaporating equal volumes of the same soil solution with and without permanganate and comparing the residues as to color, quantity of organic matter and behavior on ignition.

The method was tested by having an associate prepare a number of solutions by adding known quantities of nitrate to soil extracts containing organic matter and giving them to the writer for analysis. The results were satisfactory in every case, and the method is now used in this laboratory.

Experiments were made to find out whether nitrate is formed by the oxidation of the organic matter by the permanganate. Soil extract 1931, containing orgainc matter but no nitrate or nitrite, was treated with permanganate. No nitrate was found after the treatment. A trace of nitrite from the air was found after evaporating the alkaline solution, but none was found in the acid solution before evaporation.

A liter of a colored soil extract was heated and acidified, permanganate was added in excess to the hot solution and the brown precipitate was filtered off. The filtrate was made alkaline with sodium carbonate, divided into two parts, and evaporated. In one part, nitrogen was determined by the Kjeldahl method and in the other part by the Kjeldahl method modified to include nitrates. The same quantity of nitrogen was found in the two portions, showing that there had been no nitrate formation. This experiment was repeated with a pasture soil containing 50 per cent. volatile matter chiefly in the form of cow manure and vegetable mould. The result was the same, namely, there was no nitrate formation from the action of the oxidizing agent on the organic matter. It is therefore safe to use permanganate for the purification of soil extracts.

WEST RALEIGH, N. C.

THE DETERMINATION OF BENZOIC ACID IN TOMATO CATSUP AND OTHER FOOD PRODUCTS.

By Rodney Mott West
Received December 20, 1908.

The determination of benzoic acid is attended by peculiar difficulties in the case of many of the food products in which it is used as a preservative. Methods have been found to be unreliable, especially as applied to tomato catsups, when acceptable in their application to other food-stuffs. The semi-solid consistency of the catsup leads to the formation of emulsions during extraction with volatile immiscible solvents which can be broken only with great difficulty. A complete extraction of the preservative is thus rendered tedious and uncertain. In every instance, too, the extracted benzoic acid is so badly contaminated with more or less of a highly colored oily extract as to preclude the possibility of obtaining reliable results, either by weighing or titrating, without further purification of the acid. Numerous methods have been devised for obtaining the benzoic acid from food-stuffs in a pure state. In order to outline briefly the ground which has been covered by the various investigators their methods may be classified as follows:

I. Methods depending on the complete extraction of the benzoic acid, without previous treatment of the sample other than acidifying, and on subsequent purification of the acid in the crude extract, by
   1. Sublimation, followed by
      (a) Direct weighing or titration of the sublimate,[1] or
      (b) Collecting the sublimate in alkaline solution and subjecting to further treatment.[2]
   2. Precipitation of the benzoic acid as
      (a) Lead benzoate,[3]
      (b) Copper benzoate, or[4]
      (c) Silver benzoate.[5]

II. Methods depending on a preliminary treatment of the catsup in order to remove or render insoluble all substances which interfere with the extraction of pure benzoic acid, such as
   1. Saturating the sample with common salt and filtering,[1]
   2. Making alkaline, evaporating to dryness and extracting the dry material with ether,[2] or
   3. Distilling, either
      (a) Direct, or
      (b) With steam.[3]

None of the proposed methods falling in class I remedy the defects due to the emulsions formed during extraction. It is necessary, too, preparatory to sublimation, to dry the crude extract thoroughly at ordinary temperature, preferably in a vacuum, while the sublimation process itself requires careful attention and a large amount of time and patience for successful results. In precipitating the benzoic acid as metallic benzoates, each method presents its own difficulty, such as solubility of the benzoate in an excess of the precipitant, solubility in the alcohol used for washing, or contamination of the precipitated benzoate with foreign matter from the crude extract. By following the methods of class II, the troublesome emulsions are avoided but the method of LaWall and Bradshaw (1 under II) requires a filtration which is nearly as troublesome, which can not be accelerated by means of the suction pump on account of the gelatinous character of the suspended matter and which if carried out on the ordinary paper filter often requires several hours for its completion. Furthermore, it was found in this laboratory that the method seldom gave an extract of benzoic acid that, without purification, could be weighed with reliable results.

It is well known that benzoic acid is volatile at a temperature much below its melting point and that it distils readily with steam. Steam distillation, however, as it is ordinarily conducted, is a tedious operation and for the quantitative recovery of volatile substances a large distillate is necessary. Moreover, Hortvet[4] shows conclusively that the official method of steam distillation is entirely unreliable for a quantitative determination of the volatile acids in wine, depending to such an extent, as it does on the conditions of distillation that concordant results can not be obtained by two

[1] A. O. A. C. "Official Methods for the Determination of Benzoic Acid," Bull. 107, U. S. Dep't of Agr., Bur. of Chem. Julius Hortvet and Ralph Hoagland: Report of the Chemist, State of Minn. Dairy and Food Commission, 1907.

[2] Harry S. Reed: *Jour. Amer. Chem. Soc.*, **29**, 1626.

[3] Hager's Untersuchungen, 2 Aufl., **2**, 135.

[4] F. M. Horn: *Jour. Soc. Chem. Ind.*, **7**, 225.

[5] Hillyer: *Proceedings of the A. O. A. C.*, 1908.

[1] C. H. LaWall and H. A. Bradshaw: *Amer. Jour. Pharm.*, 171–172 (1908).

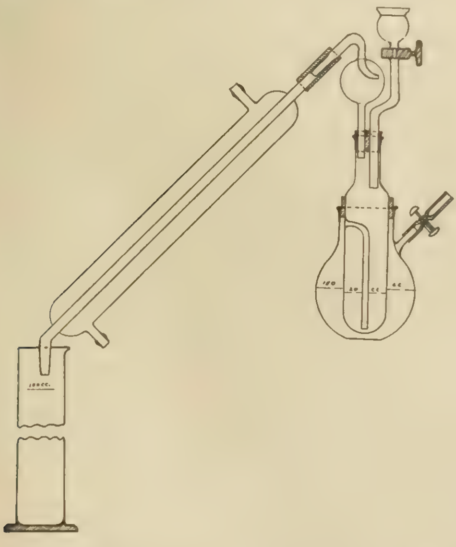
[2] A. Wynter Blyth: "Foods, Their Composition and Analysis." E. Mohler: *Bull. Soc. Chim.*, **3**, 414.

[3] Suggested by A. E. Leach, Mass. State Board of Health Report for 1905.

[4] "The Determination of Total, Fixed and Volatile Acids in Wine." This Journal, I, **1**, 31-38.

different operators or even by the same analyst using the same piece of apparatus. He shows in addition, however, that the apparatus he recommends enables a comparatively large amount of volatile acid to be carried over by a volume of distillate not so large as to interfere with subsequent operations This being true for the volatile acids in wine, it was hoped that it would prove equally true for the small amounts of benzoic acid usually found in catsup and other food products

A few slight modifications were made in Hortvet's wine apparatus (see figure). The tube leading from the outer to the inner flask was made slightly larger in diameter and was introduced half way up the side of the inner flask. This makes it possible to connect the apparatus in such a way that at the beginning of the operation the water in the outer flask will reach to the height of the contents of the inner flask. The whole apparatus was made somewhat shorter, the inner flask proportionately larger in diameter, and the outer flask was provided with a side tube closed with a rubber tube and pinch-cock by means of which the steam pressure might be relieved at any moment without danger of drawing the material under examination back into the outside flask.



Determinations with this apparatus were made on water solutions of benzoic acid of known strength in order to ascertain the per cent. of the acid recoverable, under given conditions, in 100 cc. of distillate. These results, as shown in Table I, are calculated to sodium benzoate, the form in which the acid is usually added to food products. The figures in column 2 were obtained by acidifying 10 cc. of the water solution, extracting direct with ether, evaporating the ether and determining the equivalent of the resulting benzoic acid volumetrically. The figures in column 3 were obtained similarly by extracting the 100 cc. distillate obtained from 10 cc. of the sample. In every instance the residue in the distillation flask was tested for the presence of benzoic acid with negative results. In the case of solutions 8, 9 and 10 the loss was caused by the deposition of the acid in the condenser in such large amounts that the following distillate failed to carry it all through into the receiver. The maximum weight of the acid which can be completely carried over by 100 cc. of distillate can be safely placed at 50 mg. In cases where a determination shows more than that amount the results should be checked by a second determination on half the usual quantity taken for analysis.

TABLE I.

No. of sol.	Grams of sodium benzoate in 100 cc. of sol.	Grams of sodium benzoate found in 100 cc. of sol.	Per cent. sodium benzoate recovered.	Mg of benzoic acid obtained in 100 cc. distillate.
1	0.097	0.097	100.0	8.24
2	0.194	0.194	100.0	16.47
3	0.274	0.274	100.0	23.18
4	0.374	0.374	100.0	31.72
5	0.468	0.468	100.0	39.65
6	0.562	0.562	100.0	46.81
7	0.770	0.770	100.0	65.27
8	0.979	0.972	99.3	82.35
9	1.375	1.354	98.4	114.68
10	1.440	1.411	98.0	119.56

The subjection of a sample of catsup to a similar distillation with steam resulted in indifferent success. Although a distillate was obtained which was readily extracted with ether, the extract was badly contaminated with coloring matter and volatile oils from the tomatoes and spices. In order to destroy these volatile substances, concentrated sulphuric acid was added to the catsup, prior to the distillation, in sufficient amount to thoroughly char the vegetable tissue. The distillate obtained under these conditions was free from all coloring matter and oil and was found to contain, in addition to the benzoic acid, only acetic and such other volatile acids as are readily soluble in water. The distillate was extracted with ether without the least tendency toward the formation of an emulsion and, after the evaporation of the ether, a white

crystalline residue of benzoic acid was obtained which agreed very closely both in weight and acidity with the amount of acid originally added to the catsup as benzoate of soda. Chromic acid was also tried in place of the sulphuric acid but with no apparent advantage. The method in detail for catsup follows:

About 10 grams of the sample are accurately weighed into the inner flask of the apparatus, 1.5 to 2.0 grams of paraffin added to check excessive foaming during distillation and the flask is connected with the condenser. Ten cc. of concentrated sulphuric acid are dropped in through the dropping funnel at a rate sufficient to complete the addition in from two to three minutes, the flask is gently agitated to thoroughly mix the contents and is then allowed to stand for five or ten minutes after all apparent action of the sulphuric acid has stopped. 150 cc. of distilled water are measured into the outside flask of the apparatus which is then connected as shown in the diagram, the water is slowly brought to a boil, and the boiling is continued until 100 cc. distillate have been collected. The distillate is filtered into a separatory funnel and the original receiver and filter are rinsed with two 10 cc. portions of water. Complete extraction is effected with three portions of ether using successively 50 cc., 30 cc. and 20 cc. The combined ether extracts are shaken out with water until a 25 cc. portion of wash-water requires not more than a drop of decinormal alkali for neutralization, indicating the complete removal of the water-soluble volatile acids. The ether extract is transferred to a wide-mouthed extraction flask which has been previously weighed and the ether is distilled as quickly as possible on the water-bath. At just the point where ebullition of the ether ceases the flask is removed from the water-bath, air is blown in to remove the last traces of ether, the flask with its contents is placed in a desiccator and dried over night or until constant in weight and weighed. The number of grams of benzoic acid found multiplied by the factor 1.18 will give the equivalent sodium benzoate. Considerable time may be saved, however, if the determination is made volumetrically. In such case the filtration of the distillate may be omitted as well as the weighing of the flask and drying and final weighing of the acid. The crystals of benzoic acid are dissolved in a few cc. of carefully neutralized alcohol and the solution is titrated with decinormal alkali using phenolphthalein as indicator. The number of cc. of standard alkali required multiplied by the factor 0.0144 gives the equivalent sodium benzoate in grams. The burette can be read to 0.05 cc. which is equivalent, in a decinormal solution, to 0.00072 gram of sodium benzoate. Hence, on a 10 gram sample, the results will be accurate to 0.01 per cent.

Experience with the method has shown that the following cautions should be observed:

1. The paraffin used should yield no volatile ether-soluble substance on distillation with steam under the conditions of the method described above.

2. Excessive foaming is likely to occur when the steam begins to pass into the inner flask. Careful regulation of the flame at this point is necessary. The foaming may be caused by distilling too soon after the addition of the acid, by an insufficient amount of paraffin or by an unusual amount of sugar in the catsup. A little care in manipulation will suffice in nearly every case to prevent the foam from passing over into the condenser.

3. Whenever for any reason the flame is withdrawn, the outlet tube in the outer flask must be opened or the material under distillation will be in danger of being drawn back into the water.

4. Distillation must not be carried on at too slow a rate or the condensation in the inner flask will be excessive and the results will be low. One-hundred cc. distillate should be obtained in from 25 to 30 minutes, at which rate the volume of the catsup-sulphuric acid mixture is not materially increased.

5. It has been found that, ordinarily, four 50 cc. portions of water will remove the acetic acid from the ether extract of the distillate to such an extent that a fifth 25 cc. portion will require not more than a drop of the decinormal alkali for neutralization. The acidity of the last portion should always be tested, however, and the washing continued if necessary. There is no appreciable loss during washing if care is taken that the separation of the ethereal and aqueous layers is complete before drawing off the latter.

6. The method given for the evaporation of the ether, although it requires close attention, consumes only from three to four minutes. The boiling ether keeps the temperature down to at most 40° C. The flask should never be left on the bath an instant after the ether ceases to boil or loss of benzoic acid will occur.

7. If the determination is to be made gravimetrically the ether extract should be filtered through

a dry filter into the tared flask. This will remove a large amount of the moisture with which the ether is saturated and greatly facilitate the drying in the desiccator subsequent to the evaporation of the ether.

8. The alcohol used in dissolving the benzoic acid preparatory to titration should always be neutralized just previous to its use as acidity develops on standing.

In order to test the method more thoroughly in its application to catsup, tomatoes were obtained and some catsup was made and bottled in the laboratory. One portion was kept free from a preservative; to the others were added respectively 0.10, 0.25 and 0.50 per cent. of sodium benzoate.[1] Table II shows the results obtained on these catsups. Duplicate volumetric determinations (1 and 2 in table) were made in each case. Determinations 3 and 4 were made on the same distillate: 4 is the equivalent of the benzoic acid actually weighed while 3 is the result obtained by calculation from the acidity of the weighed residue.

TABLE II

No. of sample	Per cent. of sodium benzoate added	Per cent of sodium benzoate found: By calculation from acidity of residue 1.	2	3	By calculation from wt of res 4	4 months after bottling 5.
I	0.00	0.00	0 00	0 00	0 00	0.00
II	0.10	0.10	0 10	0 09	0 09	0.10
III	0.25	0 24	0 23	0 24	0 25	0 25
IV	0 50	0 47	0 46	0 47	0 47	0.47

The general belief that during the aging of a catsup the amount of recoverable benzoic acid gradually decreases led to a further determination, four months after bottling, on each of the three samples to which the preservative had been added in the laboratory. The results obtained are shown in the last column of Table II. The figures indicate that, during four months at least, no change in the benzoate occurs which renders its recovery by the proposed method incomplete. It is conceivable, however, that reactions might take place between the benzoate and the ingredients of the catsup by means of which compounds of the acid or of derivatives of the acid would be formed which would fail to yield the benzoic acid under other conditions than the destruction of the vegetable tissue and oxidation with concentrated sulphuric acid.

Some samples of wine of known purity, to which definite quantities of benzoate of soda had been added in this laboratory, were also subjected to the steam distillation method. The results, without exception, were too low. The only way in which these low results could be explained was by the presence of alcohol, which under the influence of the concentrated sulphuric acid might contribute to the formation of ethyl benzoate. Three solutions of benzoic acid were made up by dissolving known amounts in about 10 cc. of 95 per cent. alcohol and making up to 100 cc. with water. The benzoic acid was then determined in each of these solutions by distillation and by direct extraction with ether. The results are shown in Table III.

TABLE III.

No	Benzoic acid added. gram.	Found by distillation in 100 cc.	Found by extraction of sol
1	0.08	0.07	0.08
2	0.16	0.14	0.16
3	0.24	0.16	0.24

Direct extraction in the case of the wines was found to give too high results and consequently a method based on such an extraction could not be considered reliable. It was found necessary, therefore, to dealcoholize the wine, after rendering alkaline with a few drops of a saturated solution of sodium hydrate, before subjecting to distillation. The results obtained on the wines of known benzoate content by the various methods tried are shown in Table IV.

TABLE IV

Kind of wine	Source.	Grams of benzoate soda added to 100 cc.	Grams of benzoate found in 100 cc.: By direct extraction.	By distillation without dealcoholization.	By distillation with dilute acid.	By distillation after dealcoholization.
Claret	Garrett & Co.	0.00	...	0.00	.	0 00
Claret	Same	0.11	0.13	0.10	0.10	0.11
Claret	Same	0.20	0.22	0.16	0.16	0.20
Claret	Same	0.29	0.30	0.23	0.23	0.28
Claret	Same	0.39	0.42	0.32	0.33	0.39
Sherry	Cal Wine Assn	0.58	0 58	0.42	0.48	0 58
Riesling	Same	0.29	0.32	0.24	0.24	0.29
Sauterne	Irondequoit Wine Co	0 20	0 21	0 16	0 17	0 19

In the case of substances containing alcohol, then, a convenient volume is made alkaline with sodium hydroxide, dealcoholized in the usual way on the water-bath, made up to the original volume and a 10 cc. sample taken for distillation. Where it is necessary to take the sample by weight instead of measure, dealcoholize the weighed portion as

[1] The benzoate used was assayed for purity and the necessary amount in addition to that calculated on the basis of 100 per cent. pure was added to the catsup to give the required per cent.

described and transfer to the distillation flask with as little distilled water as possible. Substances containing large amounts of fat, such as milk and milk products may be very successfully subjected to this distillation process for benzoic acid. With apple cider no difficulty was experienced when extracted directly with ether and the results were equally as good as by the distillation method but the latter is recommended as being safer in every case. A "hard" cider should, of course, be dealcoholized as in the case of wines. Jellies and jams having a high sugar content will be found to give the most trouble by excessive foaming. It will be found necessary to add the sulphuric acid very slowly and in beginning the distillation a great deal of patience will be required before the caramelized sugar is completely carbonized.

It is suggested that each analyst, before making a determination by the proposed method, test his apparatus with one or two solutions of known benzoate content and make sure that the time and other conditions of distillation are sufficient to give the desired results. In making up the test solutions for this purpose it must be borne in mind that very little of the sodium benzoate on the market is actually chemically pure. An assay of the benzoate should always accompany the preliminary tests of the apparatus.

In conclusion, the writer wishes to acknowledge the many helpful suggestions, contributing to the accomplishment of the above results, which have been made by Mr. Julius Hortvet, chief of this laboratory.

Chemical Laboratory,
State of Minnesota,
Dairy and Food Commission.

ADDRESSES.

TO WHAT EXTENT SHOULD COLLEGE TRAINING CONFER PRACTICAL EFFICIENCY ALONG TECHNICAL LINES?[1]

By Louis M. Dennis

For many years there has existed among employers in manufacturing and business pursuits a wide-spread scepticism concerning the value of the services of the recent college graduate. That this scepticism still exists is shown by the very wording of the topics that have been assigned to the distinguished speaker[2] who has preceded me and to myself. In the field of technical chemistry this doubt concerning the value of the college-trained chemist has been due chiefly to (1) the failure on the part of the employer to realize the value of chemistry in the conduct of his process; (2) the distrust shown by the "practical" man toward one whom he regards as a mere theorist; (3) the inadequacy of the training of many of the young men who have gone directly from the laboratory into technical practice; and (4) the belief on the part of many employers that if a young chemist lacks experience in their own or in allied processes, his services must necessarily be of but little value to them.

The first of these causes is rapidly disappearing, and the old commercial processes that were governed by guess work or inherited formula are suffering so seriously either through high cost of production due to waste and ignorance, or through inability to march with the times along the line of scientific development and improvement, that they are being forced to appeal to the chemist for aid in preserving their very existence. It is interesting to note this change of attitude on the part of many chemical manufacturers and to observe their rapidly growing respect for the well-trained chemist whom they had formerly looked upon as a sort of mysterious corpuscle existing in a malodorous medium and highly charged with negative usefulness.

The distrust shown by the "practical" man toward the theoretical chemist is still widely existent, but the rapid replacement in many branches of manufacturing of the man who has grown up in the works by the younger college graduate who brings into the process a sound theoretical training is evidence of the fact that the day of guess-work management is rapidly passing. We may therefore consider that the two chief causes for the feeling on the part of the employer that the recent graduate in chemistry is lacking in practical efficiency are the inadequate training of the chemist himself and the demand by the employer that the chemist possess practical experience.

Let us first briefly consider this question of the training of the chemist. There is no doubt that the scepticism of the employer concerning the value of the young chemist's services has frequently found full justification in the smallness of the benefit accruing to the employer from those services. The young graduate, however, has not been wholly or even largely to blame: the fault lies partly with those entrusted with his preparation for his calling and partly with his future employer. On the one hand, he was told by the enthusiastic but narrow-visioned teacher that early specialization in some particular branch of chemistry was essential to later success, while from the employer came the warning that he wished only such young men as had extensively specialized in that part of the college curriculum that related particularly to the employer's line of manufacturing.

There further existed in the minds of many educators and manufacturers the idea that the only use of a chemist in an industrial plant was as an analyst. What was the result? The college graduate went out into practice thoroughly acquainted with but a small portion of the field of chemistry and wholly ignorant of allied branches. Naturally he sought and by his teachers was recommended for a position in which this limited information could be utilized. If such an opening occurred he entered upon his work under what he and his employer regarded as most favorable auspices, and his progress was quite satisfactory until he began to meet problems outside of his specialty. He has been trained, let us say, as an analyst, and fails t

[1] Read before the Section on Education, American Chemical Society, Baltimore meeting, Dec. 29, 1908.

[2] Dr Wm. H Nichols; see February number This Journal.

solve a works problem because of his ignorance of physical chemistry; he has specialized in physical chemistry and is unable to test a lubricating oil; he has devoted his attention to organic chemistry and cannot ascertain the reason for the perversity of a certain reaction because of his unfamiliarity with the analysis of complex gas mixtures, or with the application of the spectroscope or microscope in chemistry. He is familiar with the main branches of chemistry but cannot advise as to the construction of new apparatus because of his inability to read an engineer's drawing; he is asked concerning the installation of electric power in his laboratory or in the works and sadly shakes his head, thereby calling to the mind of his employer the remark of Rufus Choate to the jury when he had been exasperated by repeated objections from the Bench. "You may have noticed, gentlemen of the jury, that his Honor shakes his head, but there's nothing in it." Under such circumstances it is but natural that the employer should lose faith in the college-trained chemist. In business life, it is results that count, and the graduate failed to produce them. Of course I do not here refer to the genius, for he will rise superior to the limitations of his training; nor to the weak student, for his budding aspirations should early have been blasted by a rigorous faculty.

If then the employer is to be led to look with less distrust upon the college-trained man we must first of all make sure that that training is suitable and adequate. Of course, the college cannot give the student brains, but it can teach him to use his brains. As Lorimer says: "College does not make fools, it develops them; it does not make bright men, it develops them."

The question before us here to-day is: "Can proper college training in chemistry confer upon the graduate practical efficiency along technical lines?" Before entering upon the discussion of this question, let us first seek accurate definition of it. Turning to the dictionary, we find: "Efficiency"—"that which produces results. Energetic and useful activity." "Practical" is defined as "capable of applying knowledge to some useful end." The properly trained chemist should then be "capable of applying his knowledge to the production of results." Does that imply that his college training must necessarily embrace specialization in the field that he is to enter? Not at all. In the first place it should be remembered that the student in average circumstances is able to devote but four years to his college training. All of us will undoubtedly agree that two years of general culture study before the four years of special work would be of inestimable advantage to the student in fitting him for that enlightened citizenship which should be the aim of higher education, but for the majority of the young men who enter college these additional two years are wholly out of the question. The problem that concerns the educator is, then, in this limited time so to shape the work of the future chemist as to develop mental alertness and the ability to reason clearly and correctly, and to equip the student with a knowledge of the different branches of chemistry and of allied subjects broad enough to enable the graduate successfully to cope with the diverse problems of chemical practice, and to employ in their solution the most efficient line of attack. Narrowness of training such as would necessarily result from extensive specialization during the college course would so limit the student's ability correctly to interpret his observations that graduates under this system might be likened to the blind men who were asked to describe an elephant. One felt his side and said he was like a wall; another his trunk and pronounced the elephant a snake; the third happened to seize hold of his tail and declared that he was like a rope; while others, grasping an ear, a tusk, and a leg, likened him to a fan, a spear, and a tree. Doubtless each one of us could cite many instances of false conclusions drawn by the chemist because of lack of broad information. Like the illustrious Liebig when he had isolated bromine but thought it was merely an oddly behaving chloride of iodine, the chemist of narrow training "constructs a theory" that, while it suits him, leads him far astray.

Breadth of training should be the principle underlying the college curriculum in chemistry and to make clear my views upon this subject, permit me briefly to outline the course of study that experience has led me to believe to be essential to the success of the chemist in technical practice. The elements of the leading sub-divisions of chemistry itself, inorganic chemistry, analytical chemistry, organic chemistry, physical chemistry, and industrial chemistry, should be thoroughly covered, and to these should be added some acquaintance with sanitary chemistry and agricultural chemistry. Especial attention should be paid to the instruction in analytical chemistry, for if a chemist is to succeed he must be an expert analyst. But the curriculum that offers extended courses in quantitative analysis to the exclusion of other branches of analytical work will be of much less value to the student than that which broadens his training as an analyst by affording him detailed instruction in gas analysis, organic and sanitary analysis, assaying, and thorough laboratory practice in the employment for analytical purposes of the spectroscope, the polariscope, the colorimeter, and the microscope. Although this variety of instruction along analytical lines will necessarily curtail the work in advanced quantitative analysis, yet to my mind it undoubtedly yields better results than does long practice in quantitative analysis alone. The capable student who is familiar with the scientific basis of quantitative analysis and with typical determinations will readily grasp new methods and be able to carry them through with accuracy. The equipment of the chemist should not, however, be limited to chemistry alone. He must be well grounded in certain allied lines, chief among them being physics, mineralogy, and economic geology. He should also be acquainted to some extent with the principles of construction and of power transmission. I do not mean that he should be an expert engineer, but he should be qualified to pass intelligently upon questions of construction and design and to outline to the engineer in an understandable manner his wishes and needs in the mechanical development of the process in which he is interested. For these reasons his course should further include mechanical drawing, the mechanics of engineering, a full year of work in the mechanical laboratory, and instruction in the theory and use of the dynamo.

Such a curriculum will leave the student some spare time for other work during the four years, and that can best be utilized by giving him in his Senior year a small problem to investigate. The primary object of this research should be the training of the young man in methods of investiga-

tion. By that I mean the manner in which a problem is attacked, the searching of the literature for light upon the point in question, and the exercise of his varied information in the solution of the difficulties that may arise. This undergraduate research should be carefully differentiated from the more elaborate investigation of the graduate student in which discovery is the chief end in view. If time permitted it would be of almost inestimable gain to the student to carry out more ambitious and extended investigation, for I am convinced both by observation and by the almost unanimous testimony of graduates in chemistry who have gone into technical practice, that thorough drill in research far surpasses in practical value any other of the college courses. For this reason it is most desirable that not only the prospective teacher but also the young man aiming at a technical career should, whenever possible, continue his university work until he has obtained the doctor's degree. When he then enters commercial practice, the better class of positions with correspondingly larger remuneration will be open to him, and what is of chief importance to the employer, his practical efficiency will be markedly greater than that of the student who has completed only the undergraduate course.

Toward the beginning of my remarks I stated that the demand by the employer that the young chemist possess practical experience might be classed as one of the principal causes for the existence of the idea that the college-trained chemist lacks practical efficiency. The relationship between these two may seem to be remote, but the perusal of many letters from manufacturers asking for chemists shows that employers frequently confuse the efficiency that results from suitable college training with the efficiency that follows upon long acquaintance with their particular process. If we accept the definition that "practical" means "capable of applying his knowledge to some useful end" the properly trained college graduate should show this quality at the very outset of his technical career. But his practicality must not be expected to be identical in nature with that gained by another through long experience in the works. If we give him time and opportunity the college-trained chemist will, I feel confident, develop a general practical efficiency wholly satisfactory to the employer both in quality and extent, and in the meantime, he will be able to produce results of a value sufficient to justify his retention and advancement. The confusion of scientific efficiency with works efficiency reacts in undesirable manner upon the training of the chemist, because it imbues the teacher with the idea that works efficiency is obtainable through college instruction and for that reason leads many educators to incorporate in the curriculum laboratory courses in technical processes. Personally, I believe this is a serious mistake. In the first place, the introduction of such instruction forces out of the curriculum some of what I regard to be the far more profitable lines of work above-mentioned. In the second place, the attempt to familiarize the student with a technical process by having him carry out the reactions of the procedure in a beaker or a pot cannot but fail to give him an adequate idea of the process when it is performed on a manufacturing scale. If the student is well-grounded in the theories underlying the leading commercial processes and if he has listened to lectures by experts upon the apparatus and the methods that are employed in the handling of large amounts of material, he ought to be able to grasp the details of any manufacturing process in a comparatively short time. A further unfortunate result of this point of view of the employer is that it leads him to believe that because the collegian's training has been chiefly along theoretical lines, the young man can be useful to the company only in the analytical laboratory and is unfit to be sent out into the works. I realize that the answer to this will be: "But we have tried the college-trained man in the works, and he has not 'made good'". To this I reply: "Get the right kind of a man and try again." If you are still doubtful as to his possible value adopt some such plan as that recently followed by a large manufacturing concern. They had not previously employed a chemist, but sharp competition and the desire to improve their process led them to ask us to recommend one. A young man was sent to them directly from the laboratory. The concern naturally was sceptical as to his ability to master the intricacies of their process and acting, I think, with great shrewdness, they ordered him at the outset to "go into the works and, without asking questions, steal our process if you can." He set to work and, when ready, submitted his report in writing. That he succeeded may be inferred from the fact that he soon received a hurry call on the telephone from the general manager asking him if he had kept a copy of the report. Upon replying that he always copied his letters he was ordered to tear out the copy from his letter book and destroy it at once. After relating to me his experience, the young man added: "And now I wish to make a confession. When I was a student in the laboratory I used to wonder why such a variety of work was prescribed and I often thought that a great deal of it was a sheer waste of time. I take it all back now. There was not a course in the whole curriculum that I did not draw upon in solving the details of that process."

No one realizes more fully than do I that academic theories of chemical education that are evolved in ignorance of the needs and demands of industrial practice must almost of necessity fail to efficiently equip the young chemist for a technical career. But conference and coöperation between educator and employer coupled on the one hand with willingness to shape the training to meet the requirements of the chemical industries, and on the other hand with readiness to give to the young man full opportunity to show what he can do and to remunerate him in proportion to his worth, will certainly result in distinct and far-reaching gain to our chemical manufactures and will demonstrate that the proper kind of college training does "confer practical efficiency along technical lines."

THE ATTITUDE OF TECHNICAL INSTITUTIONS TO POST-GRADUATE STUDY.[1]

By William McMurtrie.

The subject assigned to me in this discussion seems to have been somewhat mixed. I have been asked to discuss:

(1) To what extent is post-graduate training recognized or desired by employers of chemists?

(2) What should be the attitude of technical interests toward post-graduate work?

(3) What should be the attitude of technical institutions toward post-graduate study?

[1] Read before the Section on Education, American Chemical Society, Baltimore meeting, Dec. 29, 1908.

It matters little how the subject of our discussion is stated, it really becomes, what shall be the training or education of young men whose life work shall be the applications of chemistry or physics or both, in the industries. It is a question which the experience of a century at least has scarcely solved. The elements which enter into the answer are too varied, the results to be attained too mainfold, the conditions available, too perplexing, the personal equation too persistent. Shall the training be confined to the storage of the facts and laws of chemistry and physics in the minds and memories of the young students trusting to the exigencies which may arise, to find their application and that when the exigencies do arise the facts and laws will be brought forth and be wisely applied? Or shall we first cause storage of facts, principles and laws and afterward offer training in the methods whereby these shall be applied and employed in the solution of the problems likely to arise in the industries and to demand treatment with satisfactory results. Whatever may be said, the latter is what employers expect and demand. The questions which arise must be answered promptly and accurately. The amount of knowledge a man may have acquired and may possess is little appreciated unless it can be applied usefully and effectively. Complaint is not uncommon that young men from the technical schools are overeducated, overtrained; educated above and beyond the positions they must occupy and the work they have to do. While this is unfortunate in form of statement, it nevertheless expresses a fact. Many young men are profoundly educated in theories and laws and at the same time acquire little or no appreciation of the practical value of these theories and laws even in the advancement of the science to which they relate and certainly not in the solution of the problems of the industries and the arts of life. There is therefore, whether recognized or not, a demand for something beyond the regular course of study of the university or the technical school. Something beyond the mere cramming with facts and academic training, to the exclusion of the systematic utilization of knowledge in the promotion of knowledge. Here, then, is the problem propounded to the educator for solution: How shall young men be educated and trained to meet the demands likely to be presented to them by the chemical industries? In the chemical industries it is natural that a profound knowledge of chemical laws should be required but in addition to this there must be provided a sound knowledge of such laws of physics as may be necessary to the physical application of chemical laws. In the undergraduate school, first the laws of chemical action and the properties of matter, theoretical and descriptive chemistry, the methods of chemical analysis, qualitative and quantitative, must be taught, and it is well-known that one of the first steps in laboratory instruction in these methods is an introduction to the form of apparatus to be employed in the practice of experiment and analysis. Then comes the application of the laws of chemistry and of the properties of matter to the methods of operation to be used. Now since manufacturing or industrial chemistry is really analytical chemistry in a large way, similiar lines of instruction and training must apply in preparation for the industries. If acquaintance with the beaker, the casserole, the filter, the evaporating dish, the distilling apparatus, the balance must be provided in the analytical and research laboratory: if here must be taught the sources and mode of application of heat, the transfer of liquids, separation of vapors, liquids and solids, all these processes made in a small way in the laboratories must be made large in the works. Operations made in a large way must be studied and the means for effecting them made familiar. The operation of the chemist in the laboratory must become the operation of the engineer in the works. The industries demand that the men who shall control shall have some of that capacity known as engineering, shall know something of the materials and methods of engineering, of the larger apparatus to be employed and its management and have ability to apply the laws of physics in the larger operations of the works. Chemistry and engineering must therefore be combined in some measure at least, in the training of the men who will become most successful in meeting the demands of the "technical interests," and whether this is recognized generally or not, it is certainly desired by employers of educated chemists.

But the common complaint of the institutions and their teachers is, that the customary four years allotted to the undergraduate course is too brief for all that is demanded and required. Here, then, is the problem to be solved: what shall be provided in the undergraduate course or school and shall post-graduate study and training be provided and carried on under the direction and management of the educational institution, or shall the training which might be provided by post-graduate study be deferred and be supplied by actual practice in the works? How and by whom shall this very important question be answered? The demand of the present and of the immediate future, is for men who are able to work independently, to take care of the problems arising, and work them out to successful issue, with profitable result, directors in the industries and employers have little time, energy or freedom from detail, to devote to the training of young men in fundamental principles. Yet experience can be had only in practice and this must be paid for in the time, energy and material apparently wasted by young men in the earlier periods of their life work.

But the question still persists: Could the young man working under intelligent direction in the systematic application of the principles he has been taught save time? Will the work of one, two or three years under intelligent and patient training of competent teachers save time of the young man and his employers and relieve both of embarrassment, loss and disappointment?

The laudation of the German Chemical Industry has extended to all nations and is probably justified. In some of the most successful branches of the German Chemical Industry the practice is to take into the works only men who have served as "*privatdocent*" in the university or technical school, and to become privatdocent the candidate must generally have taken a course in post-graduate work in investigation and in the solution of problems, work leading to the doctor's degree. First a training for systematic applied work, then experience in teaching. The value of the latter in the preparation of young men for life work is, I believe, too little recognized. It is certainly true that one of the most excellent means of securing a thorough and fundamental knowledge of a subject is found in an effort to impart such knowledge to others.

I have said elsewhere that an important adjunct to the

successful application of knowledge is a trained imagination. Not an imagination "like the baseless fabric of a vision" nor "such stuff as dreams are made on," but an imagination based upon knowledge which furnishes a vision of what may be accomplished and suggests means for accomplishment.

So it seems to me that the proper function of the undergraduate school is to communicate knowledge of facts and methods and that the function of the post-graduate school is to furnish training in the application of knowledge to the solution of problems, to the training of the imagination and thus to meet the demands which the industries, consciously or not, are making.

A most useful beginning in such work has been made in the laboratories for research in industrial chemistry lately established in some of the leading technical institutions. Here the subjects for research, the applications of knowledge are not of an abstract but of a concrete character, and provide training in work which may produce results immediately useful in the arts of life. Here the problems arising in the industries in every-day work are solved by students, under direction of men who have themselves been trained in the solution of such problems. By such work the imagination is stimulated and at the same time trained and directed in proper channels—habits of application established which must be fruitful later on. The designers of these laboratories and the authorities who have ordered their organization and establishment, as well as the industries which have patronized and encouraged them all deserve the highest praise. It is a step in the right direction and one which must be taken in other educational institutions if the proper and most effective training of young men for the industries is to be secured.

What then should be the attitude of the industries to post-graduate work? I answer, unhesitatingly, *favorable.* What should be the attitude of the technical institutions to post-graduate work? I answer, without hesitation, *favorable.* Post-graduate work should be earnestly encouraged from both sides, from the educational and from the industrial, and particularly from the latter. It has been fully recognized in the German institutions by providing in the technical schools courses leading to the degree of "doctor of engineering," and in the university by the establishment of similar courses and providing for the same degrees. In all educational institutions the attainment of the degree of doctor—a degree not lightly appreciated nor glibly assumed in Germany—involves work of investigation leading to results, work devoted to the application of knowledge and the solution of problems. The industries in Germany are wise in choosing for their employees and directors those who have passed through the office of privatdocent and have had, therefore, experience in the training and management of men. That men may become successful without this very extended and profound training is manifest in this country and is due largely to the men themselves. But even such men would be better equipped for their work by the training provided by the undergraduate and post-graduate schools and though frequently compelled by their necessities to enter upon their life work without it they would save much labor and loss of time to have had it. Many of those who, even with limited training in the schools, have been reasonably successful in the industries and in their life work in this country have a right to speak feelingly and affirmatively upon this point.

May young men be overtrained? Surely in the laboratories and in the class-room as in the gymnasium and on the athletic field; and they may be weakened, from a practical standpoint, by their training. Yet even these are often carried by their enthusiasm to eminent success. "Fools rush in where angels fear to tread" applies equally well in the world of science and industry as elsewhere, and the struggle to get out after the rush in has produced some of the best results the world has seen, though the influence and the method may not always have been recognized or acknowledged. Each one who has had experience may furnish evidence of this fact. Effort to correct errors of one's own making often leads to splendid results. "Necessity is the mother of invention" and the needs of a man in deep trouble makes him devise means which otherwise remain dormant and without utilization. Yet errors should be avoided, and the more thorough training should lead to this.

Will the institutions meet this demand for better trained men? Will the new courses necessary to it be established? Of this there can scarcely be a doubt. The institutions are looking for the sign and will respond to it when it is plain. But what of the industries? Will the leaders make the sign prominent and clear? Will they do their share? Do they know what their share is? And do they appreciate their responsibility?

First the institutions must know what is needed and the knowledge can be acquired only by close relations with the industries. Teachers should have ready access to the industries and their work for themselves and their students. Problems should be submitted to the research laboratories and needed means and materials provided. Such coöperation must certainly lead to important progress not only in the industries, but in the related sciences and progress under such circumstances is inevitable. May the influences which control have free course and be not only justified but glorified.

THE U. S. PATENT SYSTEM: ITS USE AND ABUSE.

At the meeting of the New York Section of the American Chemical Society, held at the Chemists' Club, on January 8th, the general subject for the evening was "The U. S. Patent System: its Use and Abuse." The papers presented were as follows: F. I. Allen (late Comm'r of Patents) "Introduction: Historical and Descriptive"; W. Hastings Swenarton (of the New York Bar, late of the Examining Corps, U. S Patent Office) "Patents, Trade Secrets and Trade Names as Factors in Industrial Development—their Relative Functions;" Louis C Raegener (of the New York Bar), "Some Defects in the Practice of our Patent System and Suggested Remedies;" B. C. Hesse, Ph.D., "Some Suggestions as to Desirable Improvements;" L. H. Baekeland, Sc.D., "The Inventor's Standpoint." All of these papers, with the exception of that of Mr. Allen, who on account of illness was unable to prepare his manuscript for publication, will be published in these columns. The subject is one of great importance and is of especial interest at this time because of the reports which are coming to this country of

the operation of the new English patent law, and also because of the fact that the rules of practice of the U. S. Patent Office are at the present time undergoing revision. The following notice appeared in the December, 1908, issues of the *Official Gazette* of the U. S. Patent Office:

It is considered advisable to publish a revised edition of the Rules of Practice of the United States Patent Office, because of the changes which have been made in such rules since the publication of the last edition. In view of this fact and in order, if possible, to simplify and improve the rules governing the practice before this Bureau, I desire to obtain suggestions as to amendment of the present rules and would be glad to hear from those interested upon the subject. It is not proposed to make radical amendments to the present rules, but simply to embody such changes in or additions to the rules as will be beneficial both to the Office and to applicants.

All suggestions should be submitted prior to January 1, 1909.

EDWARD B. MOORE,
Commissioner

Nov. 27, 1908.

"PATENTS, TRADE SECRETS AND TRADE NAMES AS FACTORS IN INDUSTRIAL DEVELOPMENT—THEIR RELATIVE FUNCTIONS."

By W. HASTINGS SWENARTON.

The general conception of our laws relating to patents, is that of Statutes of Monopolies. At the present time when monopolies, not comparisons, are odious, even patents, which are often described as the only legal monopolies in the United States, are fast regaining the once notorious reputation of true monopolies, which culminated in the enactment of the famous English Statute of Monopolies. That a patent is not a monopoly (and all that can be said of patents applies equally well to Trade Secrets and Trade Names), is readily appreciated when one considers the true monopoly as recognized by the common law. According to Blackstone, a "monopoly" is defined as "a license of privilege, allowed by the King, for the sole buying and selling, making, working, or using of anything whatsoever, whereby the subject in general is restrained from the liberty of manufacture or trading which he had before." "A patent," on the contrary, to quote from Robinson on Patents, "lays no burdens upon the people, except that of remaining for a while without that which they never yet enjoyed."

When one recalls the unexampled progress, directly attributable to the inventions of American citizens, which has been coincident with the growth and development of our patent system, even long prior to this era of massive aggregations of capital, he is a poor patriot indeed if he does not thrill with pride and lose all thought of the idea of monopolies, as he approaches in turn such epoch-making inventions as the steamboat of Fulton, Stephenson's improvements in the steam engine, including the tubular boiler and the smokestack-exhaust, McCormick's harvester, Bigelow's carpet loom, the telegraph of Morse, the pneumatic process first invented by the American, Kelly, for manufacturing Bessemer steel, the Hoe press, the Otis elevator and the Howe sewing machine, the Westinghouse air-brake, the open-hearth steel process of Thomas, at last a substantial rival of Kelly's Bessemer process, the Bell telephone, Edison's incandescent lamp and the multitude of others of equal or greater importance.

In addition to the direct influence of the United States patent system, through its patents, upon the commercial expansion of the United States, it is interesting to consider at this time the report of the Commissioner of Patents for the year 1848, particularly since the United States is now recognized universally as the greatest agricultural country in the world. This report which, as is evident, was a report of the Patent Office as well as the annual agricultural report, there being no separate department of agriculture at that time, stated:

"Much complaint has been made by inventors on account of a small portion of the Patent Fund employed each year for the agricultural report, and I have heretofore sympathized in such complaint. Mature reflection, however, has convinced me that no injustice is done to the interests of inventors, by such an application of the Patent Fund, but, on the contrary, the interests of the Patent Office and of the inventors themselves have been subserved by it.

"The Agricultural report of the office, by its wide dissemination throughout the country, has contributed much to increase the reputation and influence of the Patent Office, and to spread more widely among the people a knowledge of the new inventions and improvements which have been made during the year. And thus it promotes the interests of inventors, by contributing to the more rapid introduction and sale of their machines and improvements."

The United States Patent System comprehensively protects inventions which are disclosed, through its Letters Patent, and to a lesser degree, through its caveats, or what might be termed its *letters de cachet*, or sealed and undisclosed documents. Similarly its certificates of registration more adequately secure Trade Marks to their respective owners or proprietors. Trade Marks (herein considered as a species of trade names), as well as trade secrets, in addition to the protection afforded by the United States Patent System, have long been recognized under the common law as property rights.

While both trade secrets and trade marks are of ancient origin, the legal recognition and protection, under the common law, of trade marks, long preceded that of trade secrets. In fact it is virtually but a century since the courts have extended their protecting arm to cover the property rights known as trade secrets.

The trade mark is a development of the ancient shop sign. Even the Egyptians are known to have displayed inscriptions denoting their trade in conjunction with an emblem to further indicate it. Also among the ancient Greeks signs were employed to proclaim their calling. In the ruins of Pompeii and Herculaneum discoveries are reported of representations of various kinds, let into the pilasters at the side of an open shop, as, for example, a goat by a dairy; a mule driving a mill at the baker's, and at the door of the schoolmaster's, what has been termed, "the not overtempting allurement to knowledge," comprising the representation of a boy receiving a good birching. These trade emblems were doubtless introduced into England at the time of the Roman invasion.

Originally, owing to the limited number of traders, the signs were indicative of the trade, and were employed in the same capacity as we now use street numbers. Gradually, as competition increased in these particular trades, and the shops became designated by street numbers, the

sign-board fell into disuse. Then it was that the trade mark came into active use, being merely in the beginning a transfer, so to speak, from the door of the shop to the article of merchandise.

Even the piracy of trade marks is of early origin, as witnessed by the following preface occurring in Alder's "Livy:"

"Lastly, I must draw attention of the student to the fact that some Florentine printers, seeing that they could not equal our diligence in correcting and printing, have resorted to their usual artifices. To Alder's 'Institutiones Grammaticae,' printed in their offices, they have affixed our well-known sign of the Dolphin wound round the Anchor! But they have so managed that any person who is in the least acquainted with the books of our production, cannot fail to serve that this is an impudent fraud, for the head of the Dolphin is turned to the left, whereas that of ours is well-known to be turned to the right."

A critical review of famous trade marks would indeed form an interesting lesson in psychology, and would doubtless supply a fund of useful information to the memory system doctrinaires. Without a detailed review of the multitude of priceless trade marks already in existence, a single reference to the influence of a recently adopted trade mark will possibly be of interest. The National Biscuit Company, since its formation in 1898, has extended its reputation chiefly through its trade marks, and if reports can be credited, the company attributes its commercial success to that unique example of a psychological trade mark "Uneeda."

The passage of the Pure Food Laws has been already a boon to the manufacturers of pure food, and with the maintenance of quality, their trade marks will ever stand foremost in the minds of the eighty million consumers of this country, who will, it is hoped, never again have occasion to buy standard commodities subject tot he doctrine of *caveat emptor* (let the buyer beware).

No consideration of the influence of invention upon industry can be complete without a review of the functions of trade secrets. A trade secret may comprise a process which produces an old product that is producible by other known methods in so nearly an identical condition as to prevent the determination of the method of production, even when the product is subjected to the most careful scrutiny. Such processes obviously would not include the Hall aluminum process, Kelly's Bessemer process, or Mushet's recarburizing process for the production of steel, and the Thomas open-hearth steel process. Even more recently than the above is the patented Knietsch contact process for the manufacture of sulphur trioxide. While all of these processes do not necessarily produce products that would invariably reveal whether or not a definite process was employed in their production, nevertheless each one at least requires a particular type of apparatus, of a substantially permanent nature, so that its indefinite concealment within a plant would be rendered difficult, or else the product is of a nature to indicate whether or not a certain patented process has been employed. The Bell process of telephony is another example of a process which, by virtue of the fact that substantially permanent apparatus is required to perform the same, is admirably adapted for the protection afforded by the United States Patent system through its Letters Patent.

A typical example of the type of process which one must perforce protect as a trade secret, or else dedicate to the public by virtue of the fact that it is not susceptible of patent protection, is the process of treating tin scrap, which was involved in the recent case of the Vulcan Detinning Company *vs.* The American Can Company, wherein the process in issue was apparently non-patentable, and yet extremely useful. It consisted of the employment of old processes in a system of apparatus which was peculiarly arranged as to the disposition of the various elements of the system, and also as regarded the relative distances of each element from certain other elements. In addition, apparently the size of the apparatus and the employment of a steam hammer, as one of the elements of the system, were important features. In spite of the fact that the title of the Vulcan Detinning Company to the process was clouded by virtue of its having acquired the process from parties who had surreptitiously obtained it from a German manufacturer, the court held that since there was an apparent breach of trust involved in the acquirement of knowledge of the process through a former officer of the Vulcan Detinning Company, that the American Can Company should not only be enjoined, but should account for all profits made thereunder.

No trade secret can be considered as coming under the protection of the common law unless it is really treated as a secret as such, and unless all parties who are cognizant of it, know that it is a secret, and are either employed in a confidential capacity, whereby they are stopped from denying their responsibility of keeping the secret, or are under contract, oral or written, and express or implied, not to divulge it. It need not, so far as the present status of the law on this subject is concerned, be either new, or sufficiently novel to be patentable.

The influence of trade secrets upon industry has been marked, from the earliest times. The guilds of the middle ages are famed for guarding inviolably their trade secrets. In fact, in many European countries, inventors were often compelled to hold as trade secrets and assume the risk of their secret being discovered, inventions which might have been patented, owing to the stringent requirements and high taxes imposed by foreign governments upon patents. In the great steel centers, at the present time, quite a different welcome awaits the rival steel manufacturer, in so far as obtaining access to these mammoth workshops is concerned, as distinguished from the reception which would have been tendered him but fifteen years ago. All specially built and peculiarly assembled machinery, used exclusively within the plant and not purchasable in the open market, as well as all secrets relating to the more economic production of steel, are now carefully guarded.

It is often a nice question for the manufacturer, to determine whether to protect his invention as a trade secret, or to procure a patent thereon. The mere fact that a second inventor may at any time enter the field, and apply for, and secure the grant of, a patent, is a matter of serious import and worthy of the most careful consideration. This has occurred often in the past, and for this reason, it is in some cases advisable to file a caveat in the confidential archives of the Patent Office, renewing it from year to year as its term expires, in order to prevent the issue of

a patent to a subseqeuent applicant, and yet withal avoiding the publication of the secret until such time as the competitor appears in the field. Of course the caveat should contain as full and complete a description as any patent specification, if one would insure himself against the grant of a patent to a subsequent applicant, and since most trade secrets are carefully guarded in some secret archives, commonly of a corporation, it is obvious that no rights are sacrificed by the filing of a caveat as aforementioned.

In respect of the three classes of property rights mentioned, either the manufacturer, the merchant, or the inventor, in some cases has a misconception of, or fails to realize, the protection afforded by the United States Patent System to each property right as aforesaid. The moral effect of a patent, and of a certificate of registration of a trade mark, upon the public generally, and upon competitors in particular, is often of considerable value. This is even true in the cases of what are termed "paper patents" or "paper trade-marks," that is, patents and trade-marks which are of such a nature as to be almost certain of being ultimately upset in court. When one realizes the time and money often required under the present administration and enforcement of our Patent Laws to defeat a patent or a certificate of registration, is it any wonder that corporations and individuals who are cognizant of this fact, do not hesitate to secure every possible degree of protection for their products which the common law or the United States Patent System affords them? Similarly in the case of the trade secret, there is no question but that the moral effect of a caveat upon the employees and competitors would result in increasing the loyalty of the employe and discouraging the competitor against infringing upon the rights of his rival, who had thus endeavored to protect his trade secret.

Many there are who still believe with the Examiner who was appointed to the Patent Office in 1854, and who upon resigning shortly after declared: "I believe in a little while there will be nothing for the Patent Office to do, as everything is already patented, and I am going to get out of this and engage in some permanent business." It appears to be the same old story "that familiarity breeds contempt." On the other hand, the following effective tribute, which is probably the most unbiased and spontaneous that has ever been paid to the United States Patent System, was delivered by Mr. Karekiyo Takahashi, the special commissioner appointed by the Japanese Government to gather data regarding our Patent System as practiced in the year 1899. In response to a query as to why the people of Japan desired to have a patent system, he said:

"I will tell you. You know it is only since Commodore Perry in 1854 opened the ports of Japan to foreign commerce that the Japanese have been trying to become a great nation like the other nations of the earth, and we have looked about us to see what nations are the greatest, so that we could be like them; and we said, 'There is the United States, not much more than one hundred years old, and America was not discovered by Columbus yet four hundred years ago;' and we said, 'What is it that makes the United States such a great nation?' And we investigated and found that it was patents, and we will have patents."

SOME DEFECTS IN THE PRACTICE OF OUR PATENT SYSTEM AND SUGGESTED REMEDIES.

By Louis C Raegener.

Mr. Chairman and Gentlemen:

In addressing you to-night I am taking a position somewhat similar to that of the illustrious Andrew Carnegie. After the tariff had given him personally all the protection he required, he came before the world and proved that protection for him at least was no longer necessary.

In my opinion the practice and procedure of trying a patent case is antiquated, time-consuming, abnormally expensive and generally unsatisfactory; final judgments are practically unobtainable, and pecuniary judgments so rare that any well-advised infringer need hardly fear them.

Once upon a time—so long ago that the memory of mankind runneth not to the contrary—our U. S. Supreme Court formulated rules of practice and procedure. If these rules are followed, the testimony in a patent suit can be ready for the court at the end of six months. Practically, however, it takes from a year to eighteen months to reach this point. The testimony of witnesses is taken at the lawyers' offices, usually on the typewriter. If taken stenographically, the stenographer benefits more by that method than the lawyers, because the lawyers and experts as a rule charge per diem, and of course the longer it takes, the more per diems.

The worst feature of this method of taking testimony is that it is practically legally impossible to stop either the witness or counsel from padding the record with testimony that would never be admissible were the trial in open court and questions could be ruled upon forthwith. The record is unconsciously padded in this way by nearly everybody. Firstly, it is in the direction of everybody's interest to do so; and, secondly, it requires less brain work to stuff the record than to concentrate one's thoughts upon what is strictly relevant and competent—thereby condensing the record.

It is not unusual for an expert witness to favor the court with his views on the witness stand for weeks and months at a time—and, by the way, eminent counsel once defined an expert to be one who swears expertly.

The legal taxable costs for a deposition of this kind to the successful party are $2.50. Of course this may have been a fair compensation a hundred years ago, but it does not compensate a day-laborer to-day for a day's work.

It is not at all unusual for a suit involving fairly important issues to cost each side at the rate of from ten to twenty thousand dollars per year.

After all the testimony has been taken it is printed, an oral argument takes place, printed briefs are submitted, and after the close of the arguments, if not before, the court goes to sleep, forgets the oral arguments, and after the lapse of considerable time renders an opinion resulting in a decree dismissing the complaint or directing an injunction and an accounting

There is usually a stay of the accounting pending an appeal by the unsuccessful party to the Circuit Court of Appeals for that Circuit; and if the decree of the court below is affirmed, testimony for an accounting is taken before a master, and again all the elements combine to protract examinations and increase expenses. Except in extraordinarily important cases it is best to drop the accounting. The defendant is usually an irresponsible corporation or has

lost or burned his books of account. The burden of proof is very heavily on the complainant, and the law very jealously protects the poor infringer against unjust attacks. If you are lucky you get a judgment which is not reversed on appeal; you must be still luckier if you collect it; and if the expenses of obtaining and collecting such a money judgment are less than its face value you are indeed a fortunate man.

I always believed with old Galileo that the earth does move, and if I succeeded in getting an injunction I usually had enough of my client's money by that time and was anxious to turn to the next job.

I have, however, heard of others occasionally collecting a judgment of some magnitude.

Now, having obtained your injunction in this United States, which is generally believed to extend from the Atlantic to the Pacific and from the Gulf to Canada, you might be foolish enough to think that your patent is valid and will henceforth be cheerfully respected. If you think that, you are wofully mistaken, for, mark you, there are nine Circuit Courts of Appeals of the United States of coördinate jurisdiction. For instance, the Second Circuit takes in New York, Connecticut and Vermont; but New Jersey and Pennsylvania are in the Third, and what is law in the Second Circuit in any particular case is not necessarily the law in the Third, as the latter tribunal will frequently—"always with a heavy heart, however"—intimate, when coming to a diametrically opposite conclusion from that reached by the Second.

So that if you get an injunction in New York City against the "Excelsior" corporation with a capital stock of five hundred dollars, the incorporators can go to Hoboken and incorporate as the Hoboken Excelsior Co., and everything, every detail that I have told you about the conduct of a lawsuit must be done all over again at similar expense of time and money.

The usual result is that the last Circuit Court of Appeals differs from the first, seldom that it agrees with it, and of course only when it cannot help itself. Otherwise it would surrender its own judgment, which those of you who are married all know is supposed to be wrong.

Now you are worse off than you were before. Before you began your first successful suit you could at least threaten or bluff with the patent and occasionally find an honest man who might give you a cent or two more for a patented article just so that he might feel that he was not a *tort feasor* every time, but now you are ridiculed and laughed at.

When I began the practice of the law over thirty years ago, appeals from the Circuit Court were as a matter of right to the U. S. Supreme Court. It did take two or three years before your case was reached, but when it was reached you got "a square deal" whether the decision was for or against you. It was the end—but now there is never an end in sight for the unfortunate patentee.

Some genius, who in my opinion ought to be crucified, invented the present system of appealing to the Circuit Court of Appeals and inserted a provision that no appeals from these Courts lie to the U. S. Supreme Court. It is true you can petition the U. S. Supreme Court to review a decision of the Circuit Court of Appeals, but as this august tribunal is exceedingly busy with many matters of the greatest importance most of such petitions are denied without an opinion, and the result is that whenever a diversity of opinions exists between two Circuit Courts of Appeals as to the validity of a patent, and a petition for certiorari is denied you can keep on litigating and guessing which of the two Courts is right, and the chance is one guess will be about as good as the other.

There have been attempts to create one Court of Appeals at Washington to which all appeals in patent cases would lie; but as the creation of such a court means the dispensation of patronage, I dare say that another decade or so will expire before such an improvement can go into effect.

I have narrated facts to you. How to cure these ills I am not prepared to say. In the earlier years of my practice I did not appreciate the great crime committed against the interests of the people, and now I am too old to make an effort to change them; but like Carnegie, to some slight extent I must admit that I have benefitted by these protracted and iniquitous laws.

You can readily see what such a condition of affairs leads to. As a young man I took for granted that all judges were honest and learned. I have never since had reason to change my mind as to the integrity of the judges, but the capacity and ability of judges in patent causes is as varied as the colors of the rainbow.

That patent lawyer is indeed inexperienced and careless if he does not carefully select his tribunal, so far as it is possible, for among the judges there are some who are so opposed to monopolies and patents that a mere look at the red seal and blue strings of Letters Patent incites them to such wrath that the patent is instantly doomed.

Please don't think for a moment that this is a joke, because nobody has ever yet been able to define what is invention or discovery and how much or how little genius must be shown, how laborious and how brilliant the work must be to dignify it with the name invention, and therefore any "learned" judge can always decree that the claims of the patent are void for lack of patentable novelty, and no tribunal can really settle that question in any particular case except a court of last resort like the U. S. Supreme Court.

Therefore it does make some difference whether you go before one court or another, even admitting that both courts decree according to their conscience; but after all, if the court of last resort finally finds in your favor, it is a poor consolation to say the judge meant well. It would have served your interest much better if he habitually meant ill and at the same time decided correctly in every instance.

While I have pointed out to you the abuses from which you as inventors and patentees suffer in the attempt to enforce your rights, I shall before closing call your attention to a ridiculous abuse from which of late the poor public suffers.

An infringer is called a *tort feasor*, and that is a bad enough name; but a contributory infringer is the worst specimen of humanity imaginable.

This theory of contributory infringement is, like alfalfa or Indian corn, the peculiar growth of our country, and I advise some of you patentees to cultivate this theory and profit thereby.

Under the law as made by the courts to-day you can sell your patented engines, your aluminum, your carbide and other patented products, upon condition that the purchaser, as long as he uses your patented device or process, shall

buy his flour, eggs, oatmeal or soap, his rat traps, furniture or whatever you please, from you or your agents; and if any wicked provision or hardware dealer should be mean enough to sell any of these articles to your venders with knowledge of these restrictions he becomes a contributory infringer, and you can annoy him and sue him and make him account for your losses.

This country never does anything by halves. It gives the worst protection possible to the patentee seeking to enforce the rights plainly given him by the statutory law; on the other hand, by trick and device not found in the statutory law or in the patent laws of any other country, it enables him to hamper trade in the most beautiful manner possible.

Of course this theory of contributory infringement does much to make patent laws unpopular, and in the end the honest patentee will suffer.

You might ask me what remedies I have to suggest for all or some of these evils.

I can only say that in England all patent suits are tried in open court and more quickly disposed of in consequence. The successful party recovers, say, two-thirds of his real expenses paid to lawyers and experts—but I do not profess to be accurate on this point.

In Germany, I understand, every patent is absolutely valid after five years, and during the five years practically valid unless a proceeding is brought during this period in the Patent Office to vacate the patent.

Of course neither in Great Britain nor Germany are there nine courts of last resort and of coördinate jurisdiction. The necessity for establishing one tribunal of last resort, be it a special Court of Appeals or be it again the U. S. Supreme Court, seems to me so self-evident that no man of ordinary intelligence can doubt it.

That the public would benefit by the taking of testimony before judges with some power to rule upon the evidence goes without saying, even if this would necessitate the appointment of a score or more of additional judges.

The theory of contributory infringement will probably be exploded sooner or later or confined within reasonable limits by the U. S. Supreme Court.

The abuses to which I have called your attention will undoubtedly be remedied in time, and probably by the bar itself; but you inventors are more interested in a speedy correction of these abuses than the bar, and united action on your part would undoubtedly do more to bring about the needed changes than waiting for some one else to do the work.

141 Broadway, New York,
January 8, 1909.

THE UNITED STATES PATENT SYSTEM, ITS USE AND ABUSE.

SOME SUGGESTIONS AS TO DESIRABLE IMPROVEMENTS.

By B. C. Hesse.

The United States Patent System has been so successful in the attainment of the primary object of a patent system, namely the stimulation of invention that changes therein should not be made without full consideration.

The full, free and untrammeled exercise of the monopoly granted by the Federal Government to an inventor in return for a complete disclosure to the public of his invention should be interfered with to the smallest extent consistent with full protection of the public's rights and further, the monopoly granted to the individual should be protected to the fullest extent consistent with the public's rights.

My experience has led me to the conclusion that at some points the inventor's monopoly when fully exercised tends to inflict a damage upon the public and that, on the other hand, failure of the public to make effective the monopoly granted tends to inflict, in some instances, unnecessary penalties upon inventors.

The chemist is concerned with all the subject matter which can be the object of patent protection, namely, new and useful arts, machines, manufactures and compositions of matter; fuller protection for the chemist is hardly conceivable.

When an inventor, chemist or other, obtains a patent it is supposed to be for something new and useful and he may reasonably be expected to exploit that invention so that the public can benefit by having access to it or to the use thereof subject to such restrictions as the inventor may regard as reasonable for his own protection and remuneration.

When, however, such inventor allows his invention to lie idle and without performing any useful function and without reasonable prospect thereof either by offering it to the public for its use or by acting as a protection for related inventions which he is actively exploiting and bringing to the public, then such inventor is, in my opinion, transgressing the spirit underlying the Patent System. He is reserving for himself a field of endeavor which he has agreed to exploit and is not exploiting and by his reservation is preventing its exploitation by others. To this extent he is retarding progress.

A partial remedy for this might be a low annual tax, say, $15 or $25 or some other sum not high enough to stand in the way of any invention giving any reasonable promise of remuneration yet high enough to make it appear unprofitable to many to retain reservation in fields which they are either unwilling, unable or incompetent to develop. To this extent reservation would be curtailed and the return of reservations to what might be called the "public domain" would be affected, for exploitation by the public as occasion might arise.

It would serve no good purpose, at present, to enumerate such instances but certainly all who have read the numerous patents as they appear in the *Official Gazette* have been struck with the idea that a great many patents have little or no utility, present or prospective, and many of those coming into contact with inventors and patentees have met with many cases where the ability to develop or exploit, or the ability to get others to develop or exploit is lacking or has been wholly exhausted and have also met cases where the ideas embodied in such patents could, with profit to the public, be adapted to use by others but which have not been so adapted or developed in other arts because of such patents.

When an applicant for a patent has succeeded in overcoming the objections, if any, raised to such application by the Patent Office (which is, in effect, acting for the public) it would seem reasonable that the ground covered by the patent so issued be regarded as conceded by the public to belong to the inventor and that any one contesting the legality of such reservation should be compelled to remain out of the field until he proves the contrary.

Experience, however, has led the courts to adopt a different view and in the majority of cases a patentee has to contend for the legality of his reservation, sometimes, if not generally, expending the greatest part of his energy in a litigated case in proving his title, as it were, while curtailment of the granted monopoly is going on without restraint. The reason for this seems to be that the courts have come to the conclusion that our system of preliminary examination does not, in fact, properly safeguard the interests of the public; the reasonableness of this is clear on considering the practical impossibility of any one man, or set of men of reasonable proportion, to be so fully acquainted with the entire art involved in all inventions made and operated, as to give, in all cases, a decision which is bound to be just. The remedy, therefore, would seem to lie in the direction of improving or elaborating our system of preliminary examination because I believe an absolute abandonment of preliminary examination to be necessarily vicious.

The remedy which I beg leave to suggest is that after an application has been passed to allowance in the Patent Office the public, or so much of it as is interested, be given access to the disclosure of the invention and a reasonable time within which to oppose the final grant of the monopoly, as is done in Germany, or a patent might issue subject to the conditions that if it be successfully opposed by the public within a reasonable time from the date of issue, say, one year, the scope of the patent will be diminished to the extent the opposition succeeded or revoked as the case may be; a patent obtained under either mode to be given the right of preliminary injunction in its favor and all infringement or alleged infringement thereof to cease or to be prohibited pending final adjudication of the validity of the grant.

Of these two propositions I am inclined to favor the first because so long as the grant of a patent is withheld exploitation is not likely and enterprises based upon what may be false foundations will be less likely to be started, as might well be the case under the second suggested remedy thus causing avoidable, and therefore unnecessary, losses and disappointments.

By this means the inventor, on the one hand, would receive a patent effectively shutting off infringement and consequent interference in his granted monopoly until his opponents have properly proven the illegality of the patent. The public, on the other hand, would be spared the issue of a very considerable number of patents presumably invalid and by exercising its rights to oppose the grant of patents of doubtful validity would save to itself many opportunities of endeavor and development and the expense and annoyance of proving in court the invalidity of a granted patent together with the annoyance and interference which an invalid patent is capable of producing.

In return for this, the inventor would probably be required to have his monopoly date from the date of the disclosure of the invention to the public at-large by the Patent Office, the time required to overcome the opposition by the public being very likely a proper charge against the patentee's term of monopoly.

It should be noted that it is not contemplated to take from the public the right to attack the legality of the grant of the patent but that that right remains fully open to the public throughout the entire life of the patent, subject to the condition that the patentee's rights must be fully respected until he is proven to be in wrongful possession.

This covers all the changes that I feel I should care to suggest.

There is another suggested change that is agitating a great many inventors, economists and the public generally, which is the so-called working of patents.

Personally, I am unfavorable to a compulsory working of any patents; personally, I believe that a patentee ought to be permitted to practise his invention where it best suits his convenience and the trade conditions he has to encounter; so long as he gives the public access to his invention, directly or indirectly, he has in my present opinion carried out the spirit underlying our Patent System. If circumstances are such that it is not profitable or possible to exploit the invention a patentee should not be compelled to work his patent in spite of such adverse conditions.

The foundation of the agitation for the working of patents seems to be a supposed loss of income or advantages to the public-at-large said to be due to inventions protected by United States Patents but imported from abroad, the corrective idea being that the country would be benefitted by having such patented articles or processes produced or practised within the United States. If that be the true reason then it seems to me to be foreign to the purpose and intent of the patent law and very probably antagonistic to a full and free exercise of its contemplated and proper functions. There may be other ways, perhaps by levying a special tariff on goods imported from abroad and patented in the United States, to accomplish this object, such levy to be reviewable by the Secretary of the Treasury and rescindable upon satisfactorily showing that the goods cannot be economically produced in this country. To attach a condition of working a patent, no matter how limited, under penalty of revocation or other restriction of the granted monopoly is, in my opinion, not the best way to accomplish the desired end and, I believe, not in harmony with the purposes and spirit of the Patent Law.

THE UNITED STATES PATENT SYSTEM, ITS USE AND ABUSE

THE INVENTOR'S STANDPOINT.

By Dr. L. H. Baekeland

The patent laws of the United States have been conceived with an unparalleled spirit of liberality towards the inventor. The law-giver in framing these statutes had certainly in mind to offer to the inventor the maximum of protection for his intellectual property. In no other country whatever is a patent obtainable at such a small cost; nowhere is the intended protection extended for as long a period as in the United States; nowhere is the real and first inventor so much guarded against possible disclosures or unfair indiscretion of others. In most other countries the patent laws seem to have been conceived with the main idea of bringing in a source of revenue for the government. In most of them additional taxes are levied every year which make the burden of the struggling inventor a very heavy one and seem to discriminate in favor of the rich man or the rich corporation who can afford to pay the yearly tribute.

My relations with the United States patent examiners have shown me that with very few exceptions these officials

are able, earnest and fair. They can compare very favorably with the best of all other countries. Their honesty of purpose and conduct has never been questioned by anybody except by people who instead of investigating the subject, merely limited themselves to sneering at them.

In late years one single case has transpired of a subordinate assistant examiner who seems to have tried to get appointed to the patent office staff with the very purpose of committing a dishonest act, hoodwinking the vigilance of the chief of his department. That such abuses have not occurred oftener is a real wonder when we take into consideration that the corps of examiners are an underpaid, ill-recognized, unrewarded set of fine men. Their devotion to their work with no hope of reward beyond a meagre salary is a fine example of good citizenship.

I know of many a time when views contrary to these were expressed by some impatient inventors who happened to believe that everybody in the world and especially patent examiners ought to be as thoroughly acquainted with their inventions as they themselves were. To such of my misguided friends, I must recall the fact that the patent examiner here in the United States or any other country is a man at whom are flung every day new ideas widely different in scope, in direction and in details. Many of these ideas are undigested or unclearly expressed. Other ones are the result of months and years of mature and deliberate specialization and it is hardly to be expected that a man, however open-minded he may be, should at the first glance be able to penetrate the subject as deeply as the intelligent, specialized inventor. The standpoint the examiner takes in a case where things are not very clear is that of a representative of the average uninitiated public whose interest he has to protect as well as that of the inventor. His attitude is best summed up in slang: "I am from Missouri," and it becomes the task of the inventor of "showing" and "showing why."

In several of my experiences with the patent examiners here and abroad, I have felt very thankful for the objections which were made to my texts and to my claims because I was shown either that I was not sufficiently explicit or concise, and by making the required amendments, I avoided much future trouble in the eventuality of an infringement. It may be a consolation to the United States patent examiners to know that their colleagues of other countries, for instance England, Germany and Austria, are criticized just as much by some dissatisfied and narrow-minded inventors, although their attitude is just as fair, unbiased and open-minded.

Summing up, I could hardly suggest an improvement in the United States Patent law without curtailing the privileges and interests of the poor inventor.

If I venture to make one suggestion, it would be to propose an act of reciprocity, which would consist in exacting compulsory working of all patents taken here by non-citizens of the United States and whose countries have patent laws with a clause for compulsory working which means great hardship for the American inventors who take out patents abroad.

On the other hand, it is very unfortunate that although the laws for filing and registering a patent in the United States are almost all that can be desired, I must lift my voice of protest when it comes to testing the rights of the inventor before the courts. Here the poor inventor is entirely at the mercy of a legalized system of piracy as carried out by infringers helped by all the tricks of lawyers, and let me say to the shame of our own profession, helped very often by experts who will back the lawyer to confuse an issue before a judge who most of the time is already incompetent on account of lack of theoretical or practical knowledge in the art. This game is so successfully played, that I know of rich companies here in the United States whose main method of procedure is to frighten, bulldoze and ruin financially the unfortunate inventor who happens to have a patent which he is not willing to concede to them on their own terms; that is to say, for next to nothing.

I could cite you several examples of prosperous companies where the money paid in salaries for the technical or scientific staff and for royalties is a mere bagatelle if compared to the fortunes paid annually to their lawyers who happen to look after their patent litigations.

Thus has it come about that an otherwise liberal patent law intended for the protection of the poor inventor has become a drastic method for building up powerful privileges in the interest of big capitalistic combinations

The sooner we have a special and adequate patent court to which all patent litigation can be referred and which can operate without the absurd delays and abominable expenses now involved in patent suits, the sooner will cease this arrogant frustration of the generous efforts of those who framed our patent laws.

NOTES.

PHOSPHORUS FOR THE HEMPEL PIPETTE.

The method of preparing sticks of phosphorus for use in the Hempel pipette for the determination of oxygen, as usually described, does not take advantage of a little device which suggested itself to me some years ago and which I find exceedingly satisfactory.

I proceed as usual until the liquid phosphorus is expected to solidify in the glass tube. Phosphorus is very prone to undercooling and it often requires considerable patience to await its solidification. When, however, the liquid phase is brought into contact with the solid phase equilibrium is promptly established and the column of liquid phosphorus solidifies the very instant the temperature of the normal point of solidification is reached. Contact can readily be insured because the liquid phosphorus usually protrudes slightly from the end of the glass tube and if a piece of solid phosphorus is suspended by a wire in the cooling bath one can easily bring solid and liquid together while the latter is cooling.

It will be found that this little device not only simplifies and expedites the whole operation but insures greater uniformity and far greater yield of perfect sticks.

H. August Hunicke.

MITCHELL-WALKER MOISTURE TEST.

During the past year we made investigations in rapid moisture determinations in dairy products. We personally examined a number of the tests on the market and consulted the reports of other chemists on the other tests in vogue.

The beaker test, consisting of weighing into a cup a quantity of butter, heating till foaming ceases and re-weighing, we considered a good test but open to inaccuracies when used by the ordinary creamery man. Some of its disadvantages are, the necessity of weighing very accurately, thus involving a sensitive and comparatively expensive balance; uncertainty as to the right moment to stop the heating, and to re-weigh the dehydrated butter; necessity of calculating the percentage of water from the weights.

Gray's Test involves a fragile glass contrivance and gave results from 0.5 to 1.0 per cent. too low. The test is also rather expensive to operate. The "improved" Gray's Test proved to be still more fragile and awkward to clean, but gave more accurate results due to a modification in the scale.

Other tests presented undesirable features in one form or another.

We devised a test, attempting to conform to the following requisities:

1. A rapid and reasonably accurate method. 2. An inexpensive form of apparatus both to purchase and to use. 3. A durable form of apparatus and one easy to clean. 4. A method that requires no great amount of attention or care in operating, and that can thus be used by the average factory man. 5. An apparatus that can, if damaged, be easily repaired at small cost. 6. A method equally suitable for testing butter, curd and cheese.

Our apparatus consists of a thin, copper still attached by a friction joint to an upright brass condenser fitted with a block-tin inner tube. A glass receiver reading directly in percentages and with a stop-cock near its lower end, hangs from the lower end of the condenser. This apparatus is supported on an upright brass rod to which is also attached an adjustable copper spirit lamp.

In making a moisture determination in butter, ten grams of the sample are weighed into the copper still counterpoised on a small balance. Ten cc. amyl acetate are added. The still is then connected with the condenser and heat applied by the adjustable lamp till water and amyl acetate cease to drop from the lower end of the condenser. The graduated receiver is then removed and the percentage of water read off directly at the line of demarcation between the lower layer of water and the upper layer of amyl acetate. In testing curd and cheese, five grams are used instead of ten, and the percentage read off on the scale opposite the butter scale.

For the sake of economy the amyl acetate is collected and dehydrated in the still and used over again

The average cost per test is less than half a cent. The time required for a test, including the weighing of the sample, is about ten minutes.

The test serves also for moisture determinations in such substances as oils, fats, wood pulp, bread, flour, etc.

The results obtained by this apparatus seldom vary from the gravimetric results more than two-tenths of a per cent., and usually not more than one tenth. The apparatus is simple in all its parts, and practically indestructible, since it is made almost entirely of metal.

Descriptive bulletins may be obtained upon application to W. O. Walker, Eastern Dairy School, Kingston, Ontario, Canada.

J. W. Mitchell,
W. O. Walker.

A CONVENIENT FUNNEL FOR INTRODUCING DRY REAGENTS OF POWDERS INTO BOTTLES AND FLASKS WITHOUT LOSS OF SUBSTANCE.

In order to avoid loss of small amounts of such finely powdered materials as flour, etc., when introducing them into bottles and flasks, after weighing on the balance, it has been found very convenient to make cones or stemless funnels from celluloid film. The celluloid film required should be transparent and about the thickness of a calling card. It can be obtained from dealers in art goods. A paper cone is first made of the proper size and then the celluloid is cut, using the paper as a pattern. The lap-joint along the side can be made perfectly tight and smooth by applying the proper amount of acetone to effect a softening or partial solution of the celluloid

Charles H. Briggs.

The Howard Wheat & Flour Testing Laboratory,
Minneapolis, Minn., Jan. 7, 1909.

TILLANDSIA USNEOIDES.

Tillandsia usneoides, called Spanish moss, Florida moss, New Orleans moss, long moss and black moss, is very common in Louisiana. It is an epiphyte and grows on both dead and live trees. It can be found growing on trees that have been dead for years. On trees having a dense foliage it does not grow so well, as sunlight is one of its requirements for existence.

Many people claim that it kills the trees and they regard it as a parasite. Billings[1] says that Spanish moss does not injure the trees on which it grows and he has demonstrated that it depends wholly upon air, sunlight and rain for its life.

In the winter when the pastures are poor, farmers often chop down trees and allow the cattle to feed on the moss. In order to ascertain the feeding value and the composition of this plant the following analysis was made:

Composition of Tillandsia Usneoides (Spanish Moss).

Complete analysis.

Water	69.500
Volatile matter	28 905
Silicon dioxide (SiO_2)	0.590
Iron and alumina oxides (Fe_2O_3 and Al_2O_3)	0 286
Phosphoric acid (P_2O_5)	0.032
Calcium oxide (CaO)	0.058
Sulphur trioxide (SO_3)	0 184
Potassium oxide (K_2O)	0.313
Sodium oxide (Na_2O)	0 581
Total	100.449

Feed constituents.

	Natural state.	Water-free bases.
Protein	3 68	12.07
Ether extract	1.06	3.47
Carbohydrates	15.95	52.29
Fiber	8.24	27 02
Water	69 50	..
Ash	1 57	5 15
Total	100.00	100 00

[1] *Botanical Gazette*, **38**, 99 121

Fertilizer constituents	Natural state.	Water free basis
Phosphoric acid	0 032	0 105
Nitrogen	0 588	1 928
Ammonia	0 715	2 343
Potash	0 313	1.026
Water	69 500	..

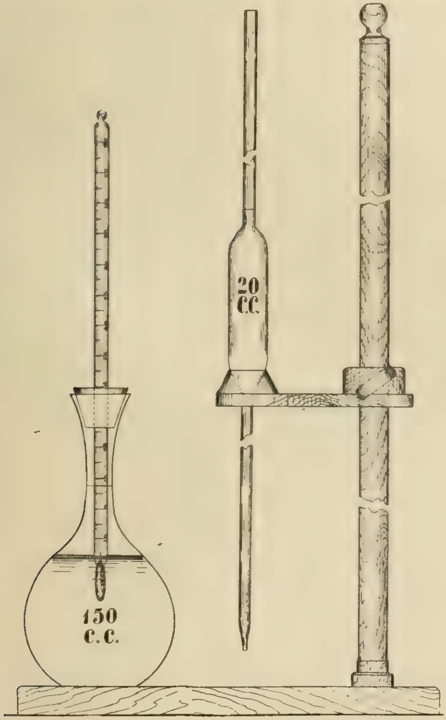
J. E. HALLIGAN.

LOUISIANA EXPERIMENT STATION,
BATON ROUGE, LA.

SIMPLE SPECIFIC GRAVITY APPARATUS FOR PORTLAND CEMENT.

Apparatus. The apparatus consists of a 150 cc. flask having a mark and the neck above flared out, a 20 cc. pipette, and a Fahrenheit thermometer inserted in a cork. The internal diameter of the neck of the flask at the graduation should not be less than 8 mm. nor more than 10 mm. The pipette is set upright in a filter stand to drain when not in use. The flask need not be accurate but the pipette must be calibrated.

Calibration.—Clean pipette perfectly, and dry. Make a mark 10 or 15 mm. above the graduation and another the same distance below the graduation. Fill to upper mark, with distilled water at 60° F. from a beaker and empty back



again. Drain 10 minutes, blow out, and fill again. Empty into a weighed flask, drain 10 minutes, and blow out into flask. The weight of water delivered is that of the volume drawn up with the walls wet. Fill to lower mark, weigh, draining and blowing out as before. The difference between the two weights is the weight of the volume between the two marks. The position of the true graduation mark is then easily found and etched or scratched on, for example:

Distance between marks	20 mm.	
Volume to upper mark	20.32 cc	
Volume to lower mark	19 76 cc	
Volume between marks	0 56 cc	
Volume for 1 mm 20 to 56	0 028 cc	
Volume of true mark above lowest mark	0.24 cc	
Distance of true mark above lowest mark	0.028	(0.24) 8.5 mm.

Use.—Fill the flask nearly to the mark with kerosene oil. Take the temperature with thermometer, remove, and make up exactly, reading the bottom of the meniscus. Wipe the inside of neck free from oil. Blow out the pipette and withdraw 20 cc. of oil from flask, draining the outside of the delivery tube against neck near mark before removing, empty and hang up to drain. Weigh out 65 grams of cement to 0.1 g. and pour from glazed paper into flask until the oil nearly rises to the mark. Use a small camel's hair brush to brush the cement with all adhering oil down the neck. Rotate flask to remove air till all the cement is suspended and cautiously add cement till the mark is reached. Rotate again, take temperature, and weigh the residue to 0.1 g. The weight of cement used divided by 20 gives the specific gravity. Correct for temperature change, 1° F = 0.01 sp. gr. When the temperature rises add the correction, when it falls, subtract. The flask can now be shaken out, rinsed with oil, and filled nearly full as before, ready for the next determination. The pipette needs only to be cleaned when cement or dust is seen on the inside.

Results.—The difference in temperature between the pipette and the oil in the flask should not be too great. The cement is usually warmer than the oil and apparatus even after standing together some time, probably due to the slow hydration of lime. The effect of the difference in the coefficient of expansion of various samples of oil is negligible. The coefficient for 1° F. is taken as 0.00050, that of glass is neglected. A sample of oil in use gave a coefficient of 0.00053 with the pycnometer, using two temperatures. In calibrating, the correction in volume for the density of water at 60° F. is practically equal to and counter-balanced the difference in volume between oil and water retained in the pipette, so that both can be ignored.

Oil retained in pipette	0 06 0 07 cc
Water retained in pipette	0 04 0 05 cc
Correction for 20 gr. at 60° F.	0.02 cc

Errors.—Any one of the following errors represents a difference of 0.01 sp. gr.

0.2 g. cement used.
0.065 cc. oil displaced.
1° F. change in flask.
6.5° F. change in pipette.
1 mm. meniscus above or below mark on flask.
0.00010 variation in coef. of exp. through 5° F. change.

FRANK GOTTSCH.

MT. PROSPECT LABORATORY,
Brooklyn, N. Y.

AN UNUSUAL INCRUSTATION ON GENERATOR COILS.

(Contribution from the Laboratory of the York Manufacturing Company, York, Penn.)

There was recently submitted to our laboratory, for analysis and explanation, a scale or incrustation of unusual character. It had been formed on the coils of pipe in the generator of a refrigeration plant built on the absorption system. The conditions in this plan of refrigeration are as follows. The generator is very similar in construction to a tubular boiler, the tubes being of two-inch iron pipe through which steam circulates. These steam coils are surrounded by strong aqua ammonia, 20° to 22° Bé. in strength, from which the heat of the steam coils drives the gaseous ammonia which is to be condensed and used as a refrigerant. The aqua ammonia comes to the generator at a temperature depending upon the cooling water used in the condenser, not often being lower than 55° Fah. and ranging at times up to 75° Fah.

The scale under consideration was formed on the outside of the steam coils and hence was deposited from the aqua ammonia and therefore represents materials dissolved by the latter. The incrustation had a maximum thickness of about one-sixteenth inch, was of an olive-green color on the outside surface, rusty from the iron pipes on the inside surface and of a somewhat varying light green on a broken cross section. Its texture presented a stony, somewhat crystalline appearance, its hardness was about 5, and its specific gravity 5.117.

The surprising feature of this material appeared upon analysis, which resulted as follows:

Insoluble matter	0.26%
Organic (oily matter)	0.59
Copper oxide	0.65
Ferric oxide	6.32
Zinc oxide	92.00
Total	99.98

It was found upon inquiry that at the plant in question some of the parts had been made of galvanized iron. The aqua ammonia coming in contact with these galvanized surfaces dissolved off some of the zinc and this in turn was deposited on the surface of the steam coils under the influence of the heat. The ferric oxide came from contact with the iron pipes.

In this connection it may be of interest to note that the action of anhydrous liquid ammonia upon galvanized and tinned iron pipe was made the subject of experimental investigation in our laboratory several years ago. The result of that inquiry, briefly stated, is that a galvanized surface is readily corroded by the ammonia while a tinned surface is but little affected.

The apparent lesson to be drawn is that galvanized iron should be avoided in all ammonia fittings.

C. H. Ehrenfeld.

TO DETERMINE FAT IN SWEETENED CONDENSED MILK.

Weigh out 25 grams of the sample, dissolve in water and make up to 100 cc. Transfer 6 cc. to a double tube milk flask provided with a small bore tube graduated to give percentage of fat for 5 cc. milk. Add 4 cc. of ether and 4 cc. acetic acid (80 per cent or more absolute acetic acid). Acetic acid of this strength will dissolve the curd but has no effect on the sugar. Place the flask in a vessel of warm water and heat until the ether is expelled. A layer of milk fat will now be seen floating on the surface of a clear and colorless liquid. Fill the flask with hot water thus raising the fat into the graduated tube. The percentage of fat can now be read, the sample whirled in a centrifugal machine and another reading made. Multiply the reading by four.

C. B. Cochran.

A QUICK METHOD FOR THE DETERMINATION OF ARSENIOUS OXIDE IN PARIS GREEN AND OTHER INSECTICIDES.

Among the numerous methods that have been suggested for the analysis of the common insecticide, Paris green, are the methods of Thorne, Smith[1] and Avery.[2]

By the use of any of these methods it is possible to obtain very accurate results. In the Smith method, however, the determination of the end-point offers some difficulty, and in both the Smith and the Avery methods, the expenditure of considerable time is involved.

The following method is presented because of its simplicity, and because of the rapidity with which it may be carried out. With the standard iodine solution already at hand, it is possible to perform the analysis within about twenty minutes, or within one-fourth of the time required for the work when either of the other methods is employed.

The details of the method are briefly as follows:

A 2 gram sample of the insecticide is weighed out and is placed in a 250 cc. measuring flask with 25 cc. of water, and 25 cc. of concentrated hydrochloric acid. The flask is then heated to a temperature of about 80° C., until the sample has dissolved, which usually requires about five minutes. Care should be taken not to heat the solution to the boiling point, since it is possible that small amounts of arsenious chloride might be lost at this temperature. After the solution has been allowed to cool, it is diluted to 250 cc., and 25 cc. portions are removed for analysis. Each of these portions is placed in an evaporating dish, is diluted with about 300 cc. of water, is treated with an excess of solid sodium bicarbonate, and is finally titrated with the standard iodine solution, using starch as the indicator. The end point in the titration may be observed most readily when a porcelain evaporating dish is used as the containing vessel. In standardization of the iodine solution, 1 gram of pure arsenious oxide should be weighed out and carried through the procedure adopted in the analysis of the sample of Paris green.

In order to compare the accuracy of the new method with that of the two others, parallel analyses of two different samples of Paris green were conducted. The results obtained are recorded in Table I.

Table I.

Percentage of As_2O_3.

Number of determination	By method of Smith.		By method of Avery.		By new method.	
	Sample A.	Sample B.	Sample A.	Sample B	Sample A.	Sample B.
1..	54.47	52.02	54.62	52.10	54.51	52.00
2..	54.53	52.02	54.58	52.08	54.51	52.00
3	54.51	52.16	54.68	52.08	54.52	52.16
4.	...	...	..	...	54.51	52.05
Ave.	54.50	52.10	54.62	52.08	54.51	52.05

[1] *J. Am. Chem. Soc.*, **21**, 769 (1899).
[2] Bureau of Chemistry, Bulletin No. 107, p. 26 (1907).

The results obtained in standardizing the iodine solution with pure aresenious oxide are given in Table II.

TABLE II.

Grams of As_2O_3 equivalent to one cubic centimeter of the iodine solution

Number of determination.	By method of Smith.	By method of Avery.	By new method.
1..........	0.002894	0.002896	0.002898
2..........	0.002894	0.002896	0.002897
3..........	0.002895	0.002896	0.002898
Average..........	0.0028947	0.002896	0.0028977

C. C. HEDGES.

CORNELL UNIVERSITY,
December, 1908.

NEW PLANTS.

THE INDIANA STEEL COMPANY'S PLANT AT GARY, IND.[1]

BY W. D. RICHARDSON.

The commencement of operations in the largest metallurgical plant which has ever been planned and constructed is an event well worth recording not only in commercial, technological and engineering literature but in chemical literature as well. While to the superficial observer it may appear that in the working of a plant such as that at Gary, mechanical problems overshadow the

Fig. 1. –Map showing location of Gary

chemical at every point, this is not strictly the case. The science of metallurgy embraces both mechanical and chemical methods, and while in the mills mechanical methods predominate, in the operation of blast furnace and open-hearth furnace chemistry comes to the fore. That the chemical operations of the blast furnace, although carefully studied for long periods of time, may yet be fundamentally improved, is well attested by the recent successful introduction of the Gayley dry blast in various furnaces throughout the country.

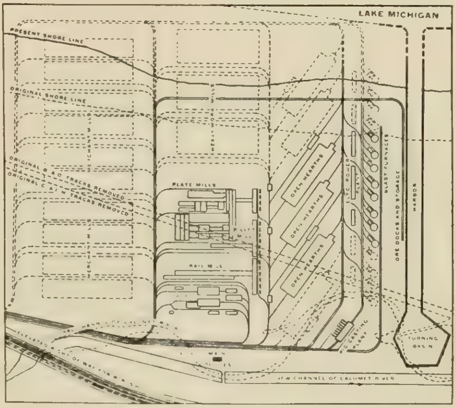


Fig. 2.—Sketch map of Gary—general plan of the new steel plant. Furnaces, mills and shops already completed or under way are indicated by solid black lines; future construction and extensions by dotted lines. To avoid confusion, duplicated railroad tracks are eliminated, the simple lines in and out of the open-hearth buildings representing six service tracks. Note how furnaces and mills have been placed to facilitate switching.

The builders of the Gary plant have done more than construct a steel works. They have in two or three years converted a waste of dune-sand and scrub oaks into a habitable region and laid the foundations of a prosperous and well-paved modern city.

The Indiana Steel Company is a subsidiary of the U. S. Steel Corporation. In 1905 the corporation set aside $10,000,000 for building the Gary works. In 1906, $21,500,000; in 1907, $18,500,000; a total of $50,000,000. No appropriation was made for 1908, inasmuch as the total amount expended even up to the present time is not greatly in excess of $40,000,000. The original announcement stated that an appropriation of $75,000,000 was contemplated from first to last. The Indiana Steel Company is a separate corporation, but is organized as a subsidiary of the Federal Steel Company. The operation of the plant, however, is carried on under lease to the Illinois Steel Company.

The President of the Indiana Steel Company is Mr. Eugene J. Buffington. The plant was designed and is being constructed under the direction of Mr. G. G. Thorp, Vice-President, Mr. A. B. Neumann, Chief Engineer, and Mr. W. P. Gleason, General Superintendent.

Location and Area.—The plant is located at the southern point of Lake Michigan, in Lake County, Indiana, about forty miles from the center of Chicago. The approximate area occupied at the present time is about 700 acres, and the area available for future extensions amounts to 1000 acres.

Water Supply.—The water supply is derived entirely from Lake Michigan, being taken from a crib one and one half miles from shore, through a six feet tunnel. The water gravitates to the pumping station, from which point it is supplied to the plant by means of horizontal-shaft direct-connected motor-driven centrifugal pumps. These are two

[1] For further descriptions, particularly of the mechanical features of the Gary plant, consult the *Iron Age*, Jan. 7th and Jan. 14th, and following numbers: The *Iron Trade Review* of Jan. 7th and succeeding numbers; *System*, Jan., '09, and *Engineering Record*, July 20, Aug. 17 and Nov. 2, 1907.

domestic pumps driven by 250 H. P. motors and two fire pumps driven by 175 H. P. motors, the combined capacity being 20,000,000 gallons in 24 hours.

Power.—There are sixteen batteries of boilers of 400 H. P. each, heated by blast furnace gas, on the plant. This gas averages in heat value 95 B. T. U. per cubic foot. Steam is used on the plant to drive two 2,000 K. W. turbines which were installed temporarily, and prior to the starting of the gas engine-driven generators. Steam is also used on the plant in auxiliary blowing engines, pumps, turbines, hammers, gas producers, etc. Of blowing engines for the blast furnaces there are eight Westinghouse and eight Allis-Chalmers horizontal twin-tandem of 2,000 H. P. each. They are operated by blast furnace gas and average 30,000 cubic feet of air per minute, each. The number planned for the complete plant is thirty-two, with a total H. P. of 64,000. The electric power plant equipment consists of horizontal twin-tandem Allis-Chalmers gas engines, direct-connected. At present seventeen of these engines are installed, with a total of 60,000 H. P., housed in a building 966 feet long by 105 feet wide. It is planned to duplicate this plant with another of the same size and this will give a total of thirty-four gas engines, with 120,000 H. P.

Fig. 3. Chemical laboratory.

Fig. 4. Pumping station.

Fig. 5.—Blast furnaces from water front.

Fig. 6.—Unloaders and ore bridges.

Fig. 7.—Ore bins.

Blast Furnaces.—Of a total of sixteen blast furnaces, each of a capacity of 450 tons per 24 hours, planned for the plant, four are operating at the present time and four are

under construction. There are four stoves to each furnace and for the eight furnaces either operating or now under construction, there are provided fourteen dust catchers. The flue dust delivered by them amounts to about two

Fig 8 —Blast furnaces under construction

carloads per furnace per day. The flue dust is not sintered. For each pair of furnaces there are provided three primary gas washers. From the primary washers the furnace gas

Fig. 9.—Blast furnaces and stoves under construction.

passes through a large main to the secondary washers. Two types of these are used, vertical tower washers and centrifugal washers, and for each furnace there are provided two of each type.

Supplementary to the blast furnace installation, a pig-casting equipment has been erected of sufficient capacity for handling the entire output of the blast furnaces.

The course of the gas after leaving the blast furnace is

Fig 10 – Furnaces, stoves and primary washers.

as follows: It first passes through the dust catchers, then through the primary washers, and after leaving the primary washers a fraction amounting to 30 per cent. of the total or 6,750,000 cubic feet per hour passes to the hot blast stoves. From the same point 7½ per cent. or 1,700,000 cubic feet per hour passes to the boiler house. The remainder passes

Fig. 11. Blast furnace showing skip incline, stoves and dust catchers. Compliments of Allis-Chalmers Co.

to the secondary washers where 2½ per cent. or 600,000 cubic feet per hour is used up. From the secondary washers the gas enters the gas holder, of a capacity of 200,000 cubic

feet. From the gas holder the gas passes by mains to the blowing engine house and the electric power station. In the former 12½ per cent. or 2,800,000 cubic feet per hour is used. 2½ per cent. or 600,000 cubic feet per hour is used for auxiliaries for blast furnaces themselves. The total consumption for blast furnaces then, exclusive of the stoves, is 15 per cent., or 3,400,000 cubic feet per hour. The remainder or 45 per cent. of the total, amounting to 10,000,000

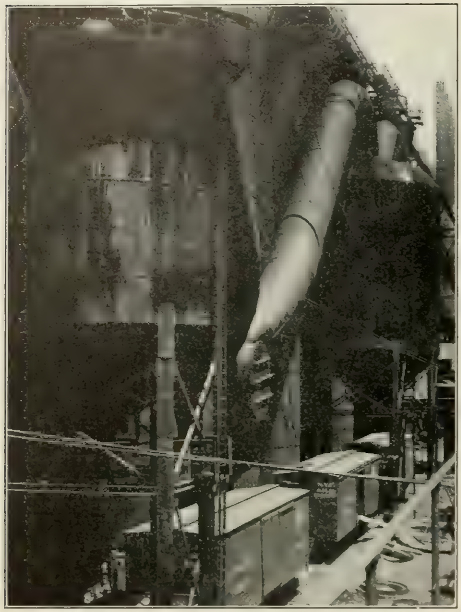


Fig 12 —Dust catchers Compliments of Allis Chalmers Co

cubic feet per hour, is used in the electric power station. The above figures are based on the production of eight blast furnaces delivering 3600 tons of pig iron per 24 hours. It is estimated that these eight furnaces will produce 22,450,000 cubic feet of gas per hour.

The Gayley dry blast has not yet been introduced at Gary.

Open-hearth Furnaces. At present there are finished twenty-eight open hearth furnaces each with a capacity of 60 tons. There are under construction fifty-six more which when completed, will give a total of eighty-four. For each

Fig 13 —Primary gas washers

open-hearth furnace are provided five Morgan gas producers. The first open-hearth plant will be in operation by the time this article is published. In the completed plant there will

Fig 14 Back of blast furnaces Gas mains leading to boiler house and secondary gas washers. Compliments of Allis-Chalmers Co.

be a rail mill with a capacity of 100,000 tons per month. This is now ready to operate. A billet mill, an axle shop,

Analyses of Iron Ores.

Ores	Fe	P.	Mn	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO	MgO.	MnO	P_2O_5	Vol	Moist
					Dry Basis. Per cent							
Chapin	59.46	0.066	0.21	5.50	1.60	85.66	1.50	3.24	0.27	0.151	2.40	..
Bernhart	56.66	0.089	0.26	13.30	1.80	80.94	1.25	0.28	0.34	0.135	2.20	..
Vermont	59.46	0.075	1.27	5.26	2.75	84.94	0.61	0.14	1.64	0.171	4.86	..
Group 4	57.58	0.063	1.10	6.20	2.53	82.26	0.50	0.36	1.42	0.144	6.66	..
Group 3	57.86	0.085	1.57	6.17	2.80	82.66	0.65	0.37	2.03	0.195	5.40	.
Vermil	65.61	0.145	0.10	3.86	1.01	93.73	0.57	0.35	0.13	0.332	0.30	..
					Original Basis.							
Chapin	56.10	0.062	0.20	5.15	1.50	80.14	1.40	3.03	0.26	0.142	2.25	6.43
Bernhart	51.59	0.054	0.24	12.11	1.64	73.70	1.14	0.25	0.31	0.124	2.00	8.95
Vermont	51.70	0.065	1.10	4.57	2.41	73.86	0.53	0.12	1.42	0.149	4.22	13.05
Group 4	49.34	0.054	0.94	5.31	2.17	70.49	0.43	0.31	1.21	0.124	5.71	14.31
Group 3	50.10	0.074	1.26	5.34	2.42	71.57	0.56	0.22	1.63	0.169	4.68	13.42
Vermil	65.04	0.144	0.10	3.83	1.00	92.91	0.56	0.35	0.13	0.330	0.30	0.87

a plate mill and a merchant mill are all under construction.

Raw Materials and Products.—The ores used in the plant will be from the Messaba, Menominee, Marquette and Vermillion districts. Average analyses from typical mines in these districts are as above, on the dry and original basis.

The ores are all delivered to the plant by the Steel Corporation's steamers. The coke used is from the Connellsville, Penna. district, and analyses about as follows:

	Per cent.
Vol	0.83
Fixed carbon	88.42
Sulphur	0.75
SiO_2	5.98
Fe	0.60
Al_2O_3	0.45
P	0.01
Mn	0.04
CaO	0.17
MgO	0.22

At the present time dolomite is used in the blast furnaces and hence the slag cannot be used for cement-making purposes. In case it is desired to produce cement from the slag, the change to calcite can readily be made. The dolomite comes from McCook, Ill., and from Gary, Ill. The following is a typical analysis:

	Per cent.
Moisture	1.50
SiO_2	0.53
Fe_2O_3 and Al_2O_3	0.59
P_2O_5	0.01
CaO	29.60
MgO	21.60
S	0.041

The coal used in the producers at the open-hearth plant is Dering No. 2 lump, from Westville, Ill., and analyzes as follows:

	Per cent.
Moisture	8.50
Volatile com	37.01
Fixed carbon	46.88
Ash	7.61
S	1.44
B. T. U	11,970

The limestone spalls for the open-hearth plant comes from the well-known quarries at Bedford, Ind. A typical analysis is as follows:

	Per cent.
SiO_2	0.63
Al_2O_3 and Fe_2O_3	0.46
P	0.008
CaO	54.90
MgO	0.51
S	0.055

Flue dust from the blast furnaces shows on analysis:

	Per cent.
SiO_2	7.63
Fe	53.88
Al_2O_3	3.51
P	0.062
Mn	0.82
CaO	0.52
MgO	0.27
C	8.36

Chemical Laboratory.—Mr. H. C. Thomas is chief chemist at the Gary plant and has been instrumental in designing one of the best iron and steel laboratories in the country. The chemical work, excepting the gas analysis work which is handled in the gas laboratory located at the blast furnaces, will be performed in one central laboratory. This is a three-story and basement brick and concrete building with 10,000 square feet of floor space. In the basement of the building are located the heating plant and power machinery for the laboratory, the acid storage, the photographic room and dark room, record room, vault and toilet room. On

Fig. 15.—Partial view of installation where 17 Allis-Chalmers twin tandem gas engines are direct coupled to Allis Chalmers generators, each unit being of 2,500 kw. capacity. Photograph taken during erection. The installation also includes 8 Allis-Chalmers twin-tandem, gas-driven blowing engines, making 25 units in all.

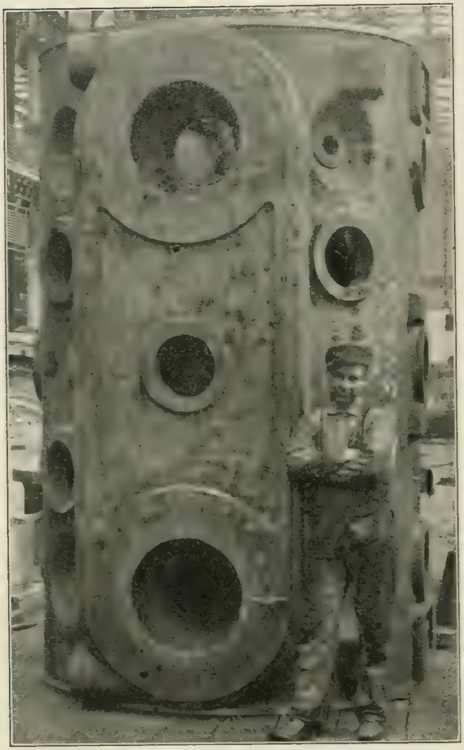


Fig. 16.—42 inch gas engine cylinder, Allis Chalmers.

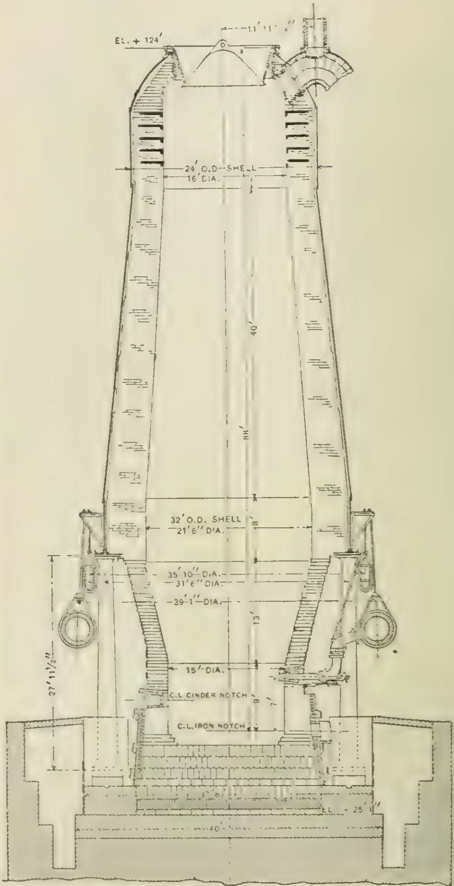


Fig. 18.—Cross section of blast furnace.

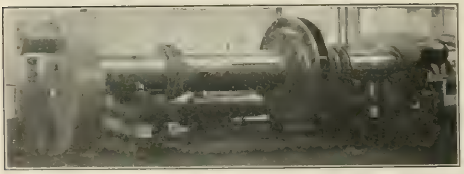


Fig. 17.—Crank shaft of 5000 H. P. Allis Chalmers 4 cycle, double acting twin tandem gas engine—weight of this part, 85 tons.

Fig. 19.—Open-hearth furnace, charging end.

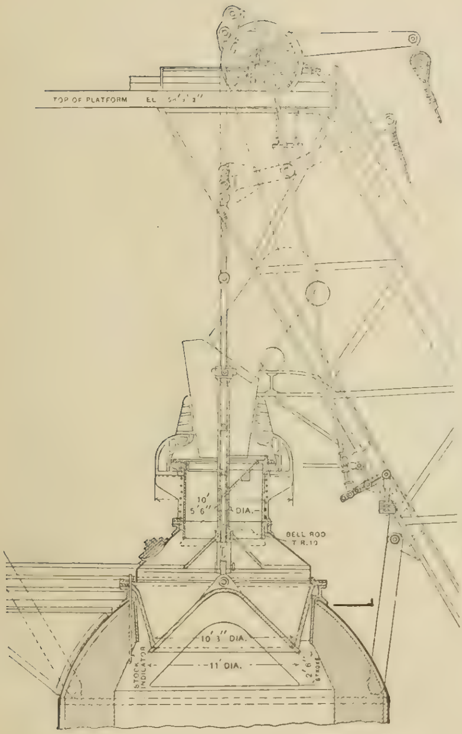


Fig. 20.—Top of blast furnace

Fig. 21.—Open hearth furnace, discharge end

Fig. 22.—View from slip.

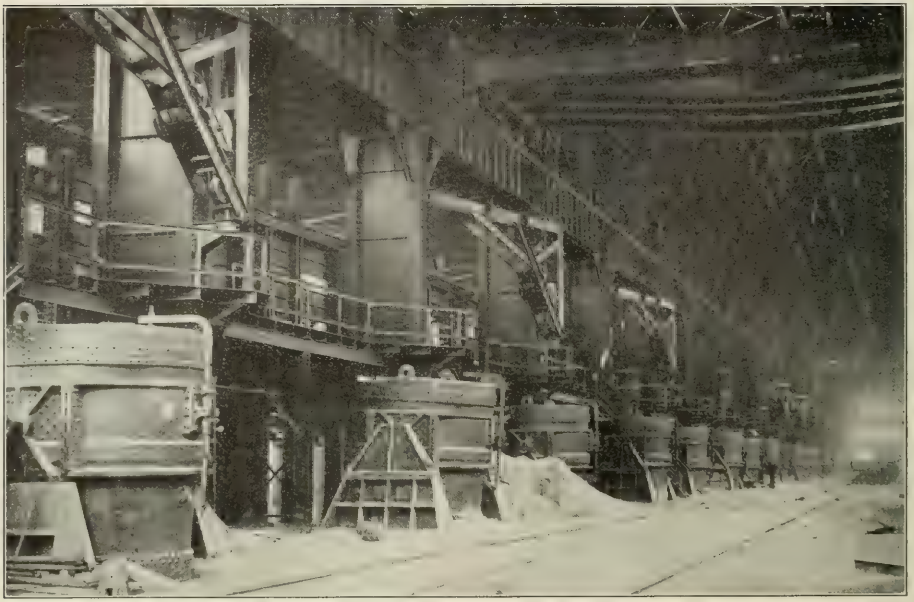


Fig. 23. Open hearth furnace, discharge end.

the first floor is the office of the chief chemist and the clerk's office, the main iron and steel laboratory, balance room and store room. On the second floor are located the laboratory for blast furnace and open-hearth materials; a laboratory for special work such as alloys, foundry work and waters; a laboratory for research work; a muffle room, balance room, store room, library, office and toilet room. The third floor is at present unfinished, but will be finished as the space is required. The building is so constructed that new stories can be added whenever necessary. No sampling is being done in the laboratory, but is handled in a special sampling plant located at the ore docks. This is a building 50 x 40 feet, containing 30 2-ton drying bins, 6 5x5 feet hot plates, 2 Allis-Chalmers grinders and one Allis-Chalmers and one Dodge crusher. Just now the sampling is performed by hand, the mechanical sampler not having as yet been installed.

The writer desires to express his thanks to Messrs. G. G. Thorp, Vice-President of the Indiana Steel Co., H. C. Thomas, Chief Chemist Indiana Steel Co., and Wm. Brady, Chief Chemist Illinois Steel Co., for the data furnished for this article.

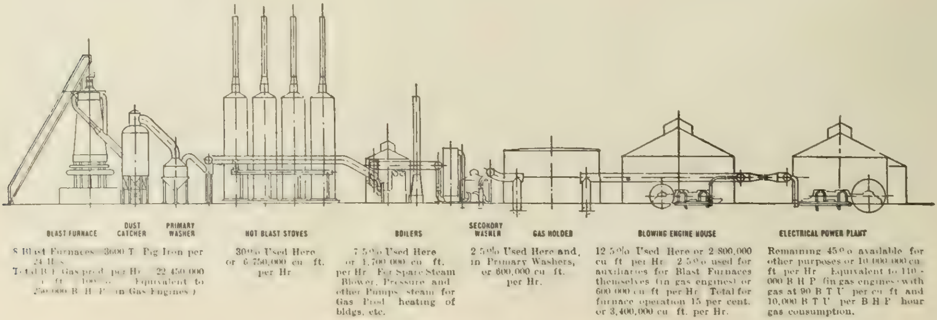


Fig. 24. Diagram for blast furnace gas.

THE FINK SMELTER.

By W. C. Ebaugh.

Much interest has been aroused in metallurgical circles by the test made with the Fink smelter at the Boston Consolidated Company's plant at Garfield, Utah. The successful operation of the experimental furnace during its trial run—when concentrates containing about twenty per cent. of copper were reduced to blister copper in a short space of time—has led the more enthusiastic and hopeful smeltermen to assert that a revolution in the treatment of fines has been effected, and that many properties that cannot be operated at a profit under present conditions will be made of value through the introduction of the new process of smelting. Whether these claims are too extravagant can be determined only after operations have been carried on under commercial conditions upon a larger scale.

As shown by the accompanying illustrations the Fink plant consists essentially of two large rotating compartments, lined with refractories, between which is a flue for the passage of the gases from one compartment to another, as well as the openings for the introduction of the fuel. These smelting compartments or cylinders are made in the shape of truncated cones placed base to base, connected at one end with the central flue and at the other with a chimney. In the plant at Garfield, which is estimated to have a daily capacity of one hundred tons, these cylinders are nine feet in length, nine feet in maximum diameter, and taper to seven feet at the ends. The lining reduces the maximum internal diameter to about seven feet. Each end of the cylinder has an opening three feet in diameter. These cylinders are rotated by friction on trunnion wheels, but in future installations it is planned to have direct gear drives in order to avoid slipping.

Fig 1 —The Fink 100 ton smelter at Garfield, Utah.
Photograph by C. W. Higgins. Courtesy of *Salt Lake Mining Review*.

The fuel is introduced through cast iron, muffle-shaped pipes that can be seen below the central flue. Either crude oil or powdered coal can be employed, and as a matter of fact the Garfield plant was built to be run with oil, but failure to obtain a supply at the time of the test resulted in a modification of the feeding mechanism so that powdered coal could be used, and this fuel was found to be satisfactory. When it is remembered that coal and coke for smelting purposes are necessarily expensive, because of the high grades required, it is evident that a furnace that can use slack coal (either anthracitic or bituminous), crude oil or even sawdust as a fuel has a distinct advantage over the ordinary smelter.

Fig 2.—Front view of the new Fink smelter.
Photograph by C. W. Higgins. Courtesy of *Salt Lake Mining Review*.

Through the top of the central flue, tuyères, that reach into the charge in the cylinder, can be introduced. These tuyères are provided with magnesia tips and are water-jacketed. Screw conveyors carry the charge from the bins through the walls of the stack compartments at the ends of the cylinders and directly into the smelting cylinders. Around the middle line of each cylinder are three tap holes for the removal of slag, matte or metal.

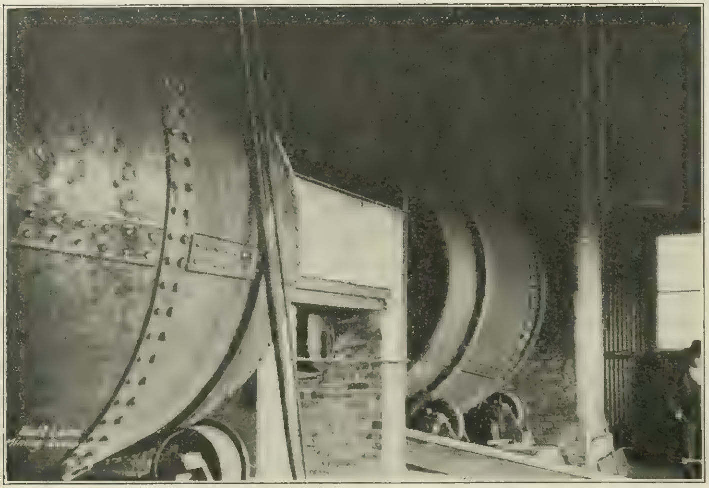


Fig. 3. Fink smelter, showing revolving cylinders and chamber
Photograph by C. W. Higgins. Courtesy of *Salt Lake Mining Review*

In the Fink smelter the inventor has applied the principle of the revolving roaster or black ash furnace, but with the important difference that in this instance there is no end fire box, the fuel being burnt in the cylinder itself. There is the additional advantage that when a bessemerizing action is wanted it is carried out in the same cylinder through the introduction of tuyères, as indicated in the preceding paragraph. It is possible, therefore, to first roast, then smelt to a matte, and finally bessemerize the matte without ever removing the charge from one cylinder. It is this economy of labor, as well as economy of fuel, that makes the new process attractive.

In operating the furnace both cylinders are in use at the same time. The ores or concentrates are fed into one cylinder which still contains the slag from a preceding bessemerizing blow. The cylinder is then rotated, and the gases from the smelting operation going on in the other cylinder are led consecutively through the middle flue, the cylinder with the fresh ore, a dust chamber, and thence to the stack. No fuel is required directly for the roasting, the sulphur from the ore and the heated gases from the other cylinder sufficing. At the proper time the charge in the other cylinder is removed, and the now roasted ore, in the cylinder with which the explanation was started, is ready to be reduced to matte. Burning fuel is blown into the cylinder, the particles of ore in the finely divided condition are quickly reduced to matte, and ordinary slag is formed. Care must be taken to regulate the composition of the charge properly and to stop the operation at the right time. If it should happen that the blow had continued too long some fresh ore or flux could be introduced and restore the charge to its desired condition. This factor of ease in regulating the various operations in the cylinder is considered as another advantage of the process. Slag is tapped through one of the three tap holes along the middle line of the cylinder, and the remaining matte is bessemerized by having the tuyères introduced through the top of the central flue, through the hole at the end of the cylinder and directly

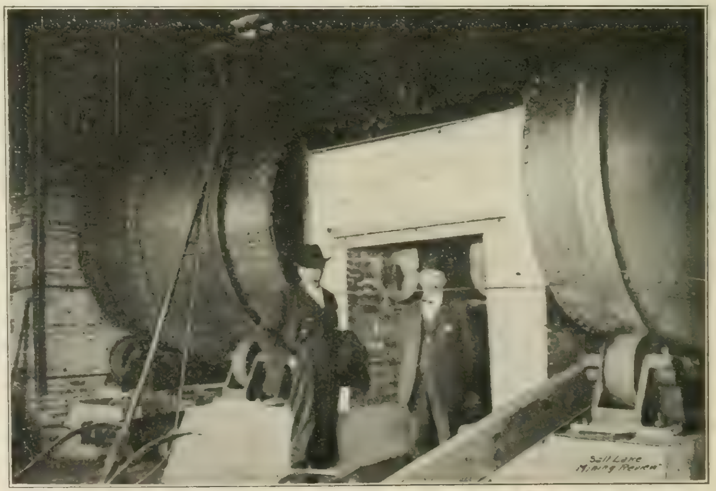


Fig. 4. Another view, showing the main working parts of the Fink smelter.
Photograph by C. W. Higgins. Courtesy of *Salt Lake Mining Review*

into the molten matte. A silica flux is added to the matte to flux off the iron, thus avoiding the excessive corrosion of the lining of the cylinder. Either a high grade of matte (white metal) or bullion can be made at will. At the end of the blow the finished product is tapped off into molds, and the superincumbent slag, which will contain more or less copper, is retained to be worked up with a fresh charge of ore.

The tests carried out with the Fink process have been declared successful. Samuel Newhouse, whose word concerning metallurgical and mining matters carries weight, is quoted in the press as follows: "You are now at liberty to say for me that the Fink process of smelting ores is a demonstrated commercial success. You can make the statement just as strong as you like. * * * There is no question of its amounting to a revolution in the art of smelting; it is a triumph in the science of metallurgy that must command world-wide attention. The process will be the means of making mining profitable in hundreds of places and under innumerable conditions where and under which profit-making is now impossible." (Signed interview by Samuel Newhouse in the Salt Lake City *Herald* of January 18th, 1909.)

The advantages claimed for the process are: (1) that fines and concentrates can be smelted without preliminary treatment; (2) economy of fuel, for roasting is carried on by the aid of waste heat from the smelting operation, and either slack coal or crude oil can be used as fuel; (3) prevention of the loss of fines, for the green ore is not subjected to a blast while it is dry, but is run into the residual converter slag from a preceding operation; (4) complete conversion of ore into metal without removal from one compartment; (5) convenience for use in either intermittent or continuous smelting, thus adapting it to the small producer and to places where the ore supply is irregular; (6) repeated use of the furnace without relining; (7) low cost of installation.

Opposed to these advantages one must consider the following objections to the process: (1) its inability to compete with present blast furnace and reverberatory practice in handling large tonnages of ore obtainable in a regular supply; (2) that the desirability of trying to carry out three different such operations as roasting, smelting and bessemerizing in one piece of apparatus is open to question; (3) the possibility of obtaining clean slags without using some form of settler; (4) that the introduction of raw ore into a cylinder containing a mass of bessemer slag would result in a loss of roasting efficiency.

Until long runs are made under conditions that approximate those that are encountered in practice, judgment as to the cost of operation cannot be made with accuracy. It is said that such tests are to be carried out as soon as possible at Garfield and at the Cactus plant of the Newhouse Mines and Smelters Company.

University of Utah,
January 29, 1909.

QUOTATIONS.

(From *Schimmel's Semi-Annual Report—Fall* 1908.)

PEPPERMINT OIL, AMERICAN.

We have again received a detailed report from our New York branch, whose expert has visited this year, as usual, all the peppermint districts. We abstract the following from this interesting information:

(1) WAYNE COUNTY, NEW YORK.

The area cultivated with peppermint is this year confined chiefly to the districts of Arcadia, Lyons, Sodus, Marion and Palmyra, while Williamson, Junius and Galen, as shown below have only very small plantations. The cultivation continues to decline from year to year, as all hopes of a permanent revival of the peppermint oil prices have after the experience of the last few years, been abandoned almost everywhere, and it is found more remunerative to grow wheat, buckwheat, sugar-beets, beans, or peas on the fields, and lately also willows for the manufacture of baskets. The bulk of the peppermint harvest this year is two years old, and experience shows that the quality of the oil in such case cannot exactly be called first-class. No less a quantity than 20,000 lbs. peppermint oil from last harvest is still unsold in the hands of the farmers, who are reported to be determined to hold back also the bulk of the new product, if better prices than in 1907–8 cannot be obtained this season.

The area under cultivation is made up as follows:

	This year's (1908)		Last year's (1907).	
Williamson ...	2	acres	4	acres
Marion ...	10	"	40	"
Palmyra ...	13½	"	18	"
Sodus ...	13	"	20½	"
Arcadia....	43	"	113	"
Junius ...	3	"	11	"
Galen. ...	6	"	10	"
Lyons...........	31	"	40	"
	121½	"	256½	"

The falling off in the cultivation is clearly shown by these figures.[1]

The result of the distillation of the whole area may be probably taken as follows:

121½ acres at 30 lbs. average................	3645 lbs.
257½ acres at 12 lbs. average..............	3090 lbs.
	6735 lbs.
Add to this stocks amounting to about........	23000 lbs.
Makes a total available quantity of about......	30000 lbs.

It follows that in spite of the great shortage in the cultivation, there will be no scarcity of this oil, for the above quantity may be described as absolutely normal.

(2). MICHIGAN AND INDIANA.

In these districts also the distillation has to fall back chiefly on peppermint of last year's growth, as, owing to abundant rains in the spring, new plantations could be laid out only in a very few places. On the whole the fields are very weedy, so that the distillation material also leaves much to be desired. The stocks of 1907 oil are here also very considerable; our informant speaks of about 46,000 lbs., while others even mention 75,000 lbs. as having been held back by the farmers. The harvest is rather late this year, so that a second cut was out of the question.

The production of this year may bring the stocks still on hand to a quantity which approximately equals that available last year—as is the case in the state of New York—but the opinions of individual observers differ considerably on this point. Owing to the low prices the farmers in Mich-

[1] *Comp. Report*, Oct., 1907, **69**.

igan and Indiana have also resolved to grow very little peppermint next year, or none at all.

The following areas are under cultivation:

	This year's (1908)	Total area (1907).
Michigan —		
Berrien Co	281 acres	1401 acres
St Joseph Co	250 "	1020 "
Branch Co	65 "	215 "
Kalamazoo Co	25 "	75 "
Van Buren Co	125 "	920 "
Allegan Co	195 "	1685 "
Eaton Co	30 "	735 "
Cass Co	45 "	185 "
Indiana—		
South Bend	...	200 "
Mishawaka	130 "	585 "
Osceola	74 "	450 "
	1220 acres	7471 acres

The peppermint oil trade in the United States has suffered during the last few months from severe depression; the general state of business was little inviting to speculative enterprise, and a large number of the well-to-do farmers having, as already stated, made up their minds not to dispose of their oil at the present low prices, the market was as quiet as possible. Only a very few transactions took place; and, contrary to what was usual in former years, it happened very rarely that any large parcels changed hands repeatedly already on the American market. For this reason it is all the more surprising that the European trade in this article during the last half-year was exceptionally brisk.

BOOK REVIEWS AND NOTICES.

A Short Pharmaceutic Chemistry, Inorganic and Organic. By I. V. Stanley Stanislaus, M.S., Ph.D., Professor of Pharmacy and Organic Chemistry and Dean of the School of Pharmacy of the Medico-Chirurgical College of Philadelphia, and Charles H. Kimberly, B.S. (in Pharmacy), Ph.D., Professor of Applied Chemistry in the School of Pharmaceutic Chemistry of the Medico-Chirurgical College of Philadelphia. Second Edition. P. Blakiston's Son & Co. Philadelphia. 1908. 610 pages. Price, $2.50 net.

The authors of this book are teachers in a school of pharmacy and presumably have had in mind the needs of students in schools of this class. It must be admitted that the presentation of the elements of chemistry to beginners in such schools is a difficult matter, as the young people usually enter upon their work with a relatively low intellectual equipment. Books for their guidance should be simple and clear, and need not be very extensive in scope. The aim should be to impart a knowledge of principles, rather than to present a great array of facts, however interesting and important the latter may finally appear. In the presentation of facts the book before us has gone far enough, possibly too far. But in the proper presentation of the foundation theories of general chemistry it is, in the opinion of the reviewer, very weak. The absurd paragraphs headed "The Ionic Theory" (p. 178) and "Physical Chemistry and Electro-Chemistry" (p. 179) are good illustrations of the authors' acquaintance with modern chemistry. Such awkward statements as this (p. 18) are not uncommon:

$$H_2O + \text{electrolysis} = H_2 + O.$$

Acids are treated as a group, without regard to their composition, and hence we find (p. 68 to 71) this order of paragraphs: nitrous acid, nitric acid, hydrocyanic acid, hypophosphorous acid, metaphosphoric acid, hydrochloric acid, nitromuriatic acid and the chlorine oxyacids. On the following pages we find dibasic, and then tribasic acids in a similar order.

The authors seem to feel more at home in the field of organic chemistry as they devote much space to wonderful graphic formulas. These look well in print, and impress the student. But think of the graphic formulas for chrysamine, Biebrich scarlet and crystal violet for beginners ! ! ! (pages 447 and 466). Of any proper appreciation of logical system there is but little, while ambiguous and inaccurate paragraphs like the following are common enough: "Substances which give reactions of two classes of substances are termed 'tautomeric' " (p. 395). On page 483 we find this bit of wisdom: "Benzoic acid is used as a preservative in foods, but its use should be prohibited, in that it is converted into phenol by the liver and acts as a systemic poison."

The book is full of typographical errors, some of which are listed in a table. But enough blemishes are left to condemn it, even for the overworked and not very particular pharmacy student. J. H. Long.

Chapters on Papermaking. Vol. V. Clayton Beadle. London: Crosby, Lockwood & Son. 1908. Small 8vo. pp. 182.

The present volume which is the fifth in the valuable series of which Mr. Clayton Beadle, the well-known English authority on papermaking, is the author, concerns itself with the theory and practice of "beating," which operation is aptly termed "the very centre of papermaking." The work of the Hollender or beating engine in opening out, bruising and shortening the fibers which are later to form the sheet and which have already undergone the preliminary mechanical and chemical processes of purification, is perhaps the most important operation in the whole art of papermaking, and the one which demands, if fine papers are to be produced, the highest degree of intelligence and discrimination in its direction. It is in fact a mill proverb that the paper is made or spoiled in the beater. In view of this it is a matter of surprise that papermakers generally have given so little attention to the underlying principles of this portion of their art and a subject for congratulation that so capable an investigator as Mr. Beadle has now devoted himself to their consideration. The volume in which his conclusions are recorded should be in the hands of every papermaker, and in the library of every chemist whose work has to do with papermaking. The studies, by dynamometer and direct-connected motors, of the amounts of power consumed by different types of beater during the several stages of the operation, are of especial interest even though their general application is necessarily limited by the great extent to which the several factors concerned in the problem may vary in different mills.

The advantages offered by stone beater rolls, so largely used abroad in the preparation of stock for grease-proof and translucent papers, have never been appreciated in this

country. The relative merits of stone rolls and metal bars are here discussed at length. Attention should also be called to the studies of the length and condition of fibers at different stages of beating, and to the methods described for ascertaining the suitability of beaten stock for dense or bulky papers as the case may be by determination of its "wetness."

Although the text of this new volume is deserving of much praise, the same cannot be said for the illustrations which accompany it. These are generally of too small scale and from plates so worn that the impression is ragged and indistinct. A number of equally unsatisfactory photomicrographs of fibers are reproduced.

ARTHUR D. LITTLE.

The Methods of Textile Chemistry. By FREDERIC DANNERTH. New York: John Wiley & Sons. 164 pp. Price, $2.00.

From its title-page this little volume purports to be "the syllabus of a lecture course adapted for use in textile laboratories." By the latter term the author doubtless intends to signify the laboratories of textile *schools* rather than the general sense of laboratories in textile establishments, as these would scarcely permit of the delivery of a lecture course. The volume, though rather sketchy in character, contains some valuable matter, and in many cases is nicely systematized. In other cases, however, it rather states the problem than attempts to solve it; for instance, in a section on the "detection of mordants on the fiber," the author states that "the ignition method is found to be preferable. * * * The ash may contain aluminium, chromium, iron, manganese," etc., etc., but the student is left in the dark as to *how* these various substances may be detected. Further, "phosphates are detected by means of the ammonium molybdate reaction," but no hint is given as to what this reaction is or how it is carried out. Again, "tin compounds are looked for in the ash as given above;" on looking "above" we find the only reference to be "the ash may contain tin." In another section on the "detection of sizing on a fabric," the student who seeks for information on the subject is met by the rather unexplanatory statement that the "metals which may be present are magnesium, calcium, and zinc." No attempt is made to furnish a method for the proper detection of these substances. In the same section we are told that Irish moss may be detected in a sizing by the fact that it "gives no precipitate with the usual reagents"—a rather hopeless state of affairs. If the author had taken the pains to describe the "methods" which the title of the book would suggest, it would have far more value, but in the majority of instances, he merely states conditions or problems, and offers no method for their solution.

Another feature in this book, which we also believe to be common to many books of its class, is the mixed nature of the spelling employed. In some places we find "aniline," in others "anilin;" the author insists on "benzin" and "diphenylamin," but also gives us "chlorine," "iodine," etc. This is a transition period in the question of spelling chemical names, but an author should adopt either one side or the other, and adhere to it rigidly—or at least throughout one book.

On page 86, of this book, the figures given for the strength of cotton yarns would lead most readers astray; for instance, under 40's twisted American yarn, the average number of fibers in the cross-section of the yarn is given as 100, the strength of each fiber is stated as 140 grains; hence the calculated strength of the yarn is 160 pounds (*sic*). To the uninitiated this seems a rather remarkable calculation; though some solace is furnished in the further statement that the actual strength is only 36 pounds, yet even this figure would indicate that the 100 fibers acquired a marvelous increase in strength when spun into yarn. The author has omitted to state that the calculated and actual strengths of the yarn are based on a lea of 80 threads.

J. MERRITT MATTHEWS.

Tonindustrie-Kalender, 1909. Part I, Calendar; Part II, pages 406; Part III, pages 212. Berlin: Published by the Tonindustrie-Zeitung.

The first part of this work is merely a calendar, with spaces and blank pages for memoranda, and is satisfactory for the purpose, except that it might be just as well to omit the bright green pages devoted to advertising matter distributed indiscriminately through the volume. The third part consists of a classified book index and also contains an index of machinery manufacturers and dealers in materials of interest to the clay industries. The second part contains a large amount of information in connection with the raw materials, manufacture, analysis and testing of materials and products of the clay industries, a useful pocket companion to either the chemist or superintendent in the ceramic industry.

W. D. RICHARDSON.

American Handy-Book of the Brewing, Malting and Auxiliary Trades. By ROBERT WAHL and MAX HENIUS. Third edition. Two volumes. 12mo. flexible leather. pp. 1596. Chicago: Published by Wahl-Henius Institute. 1908. Price, $12.00.

This is a compendium of general and special information for the use of brewers. The first edition was published in 1901, the second edition in 1902. In the present edition several new chapters have been added and most of the old have been entirely rewritten with a view of bringing the work down to date. Volume I takes up the following subjects: Physics, Mechanics, Electricity, Power, Lubricants, Mensuration, Weights and Measures, Mathematical Tables, Chemistry, Brewer's Chemical Laboratory, Botany, Microorganisms, Brewer's Microscopical Laboratory, Legal Relations and Bibliography. In the chapter on Power, the following divisions are covered: steam boilers, combustion, pumps, steam engines, steam turbines, gas engines, transmission of power, air compressors, refrigeration, heating and ventilation, and dynamic electricity. Volume II takes up the malting and brewing processes proper, as follows: Brewing Materials, Barley, Malthouse, Malting Process, Brewery Buildings, Brewery Outfit, Diastase and Peptase, Yeasts, and Fermentation, Pure Yeast Culture, Brewing Operations, Utilization of By-products, Brewery Calculations, Beer Standards, Miscellaneous Information, Dictionary of Technical Terms in German and English. Under Brewing Operations are to be found the following subdivisions: fermenting cellar operations, special brewing systems, special American bottom-fermentation beers, production of thick-mash beers in Germany and Austria, chip-fermentation beers in the United Kingdom, America and Germany; combination of various beers, brewing losses

from malt mill to platform, bottling of beer, treatment and protection of surfaces, and treatment of boiler water. The work is all the name implies and in point of usefulness may be compared to Kent in the engineer's library, or to Chemiker-Kalender and Lunge's pocket book, in the chemical laboratory. The printing, paper and binding are excellent and the index comprehensive. W. D. RICHARDSON.

Handbook for Cement Works Chemists. FRANK B. GATEHOUSE. J. B. Lippincott Co.: Philadelphia. Price, $1.75.

The author is chemist to the Dartford Cement Works, England. It is a work intended to serve a double purpose, namely, a guide to chemists without extended experience and at the same time a valuable reference book for the experienced chemist. C. N. WILEY.

Factory Glazes for Ceramic Engineers. By A. WEST, Riding Expert. E. and F. N. Spon, Ltd., 57, Waymarket, London. Price, 42 s. net.

Glazes for the temperature "of the soft porcelain kiln," using the following constituents: feldspar, Cornish stone, whiting, barium carbonate, oxide of zinc, china clay, and flint. Unfavorably reviewed in *Brit. Clayworker*, **17**, 241–2. H. E. ASHLEY.

An important volume upon "The Design, Construction and Maintenance of Sewage Disposal Works," by Hugh P. Raikes, has recently appeared in England. (D. Van Nostrand Company, New York.) The problem of Sewage Disposal is one which is receiving necessarily much attention in this country, and which is certain to be an increasing factor in the well-being of all thickly settled communities. This work, therefore, of Mr. Raikes is a valuable manual and as it is a practical and complete treatise it will certainly demand the attention of our civil engineers generally as well as the municipal officers of our towns and cities. It forms an 8 vo. volume of over 400 pages, well illustrated, and price, $4.00, net.

Dr. George F. Lunge, the well-known author of the standard work on "Sulphuric Acid, Ammonia," etc., which has been translated into English, also author of "The Alkalies Makers' Hand Book," in collaboration with the late Dr. Ferdinand Hurter, has recently prepared a new and revised edition of this latter work under the title of the "Technical Chemist's Hand Book." Practically, this may be stated as an entirely new work, inasmuch as the additions and the general revision have been so extensive and thorough. A more complete treatment of the subject matter was published in the German, in 1904–5, and a translation of this, edited by Dr. Chas. A. Keane, is in course of publication under the title of "Technical Methods of Chemical Analysis," of which volume 1 (in 2 parts) has appeared (price, $15.00). The publishers in this country of these works are "The D. Van Nostrand Company."

Prof. S. P. Thompson has in preparation a new book on "The Electric Production of Nitrates from the Atmosphere." There are no important works on the subject at present and the new volume will be welcomed by the many engineers and chemists interested, especially as Prof. Thompson has taken a foremost part in the investigations carried on along this line. Two German works have previously appeared on this subject: Donath and Frenzel, *Die technische Ausnutzung des Atmosphärischen Stickstoffs*, 1907; and Vageler, *Die Bindung des Atmosphärischen Stickstoffs in Natur und Technik*, 1908.

Salter's translation of Gregorius's Manual on "Mineral Waxes," is somewhat important as the very scanty literature, at least in English, on the subject is apparent. The manufacturing industries, however, in the line of paraffin, ceresine, and more recently mineral wax, rank among the important branches of technical chemical production, and therefore this work will probably prove of value to all those engaged in such industry. Price is $3.00, net.

NEW BOOKS.

Anleitung zur mikrochemischen Analyse der wichtigsten organischen Verbindungen. By H. BEHRENS. (4 Hefte) Heft 2: Die wichtigsten organischen Faserstoffe. 2. Aufl. Hamburg, 1908. 8vo. mit 3 Farbendrucktafeln u. 20 Figuren. Price, M. 5.

An Introduction to Pharmacodynamics Based on the Study of the Carbon Compounds. By F. F. and J. M. BRICKDALE London: Edw. Arnold. 1908. pp. 372. Price, $4.

Traité d'Analyse chimique quantitative. By R. FRÉSÉNIUS. Huitième édition français. 1652 pp. 430 fig. 18 fr. Lib. Masson et Cie. Paris. 1909.

Handbook for Cement Work Chemists. By F. B. GATEHOUSE. Philadelphia: J. B. Lippincott Co. Price, $1.75.

Laboratory Outline for Determinations in Quantitative Chemical Analysis. By ALBERT F. GILMAN. 1908. Easton, Pa.: Chemical Publishing Co. Price, 90c. net.

Text-book of Medical Chemistry and Toxicology. By J. W. HOLLAND. Saunders. Price, $3.00 net.

Die Pharmokologie eine biologische Wissenschaft. By C. JACOBI. Leipzig. 1908. 8. Price, M. 1.50.

Agenda Dunod pour 1909: Chimie a l'usage des Chemistes et Ingenieurs. By EMILE JAVET. 400 pages de texte et 128 pages blanches pour notes. 2 fr. 50. Lib. H. Dunod et E. Pinot, Paris, 1909.

Die Chemie im täglichen Leben. By LASSAR-COHN. Gemeinverständliche Vorträge. 6 Aufl. Hamburg. 1908. 8°, 352 Ss. 24 Fig. Price, M. 4.

L'Evolution souterraine. By E. A. MARTEL. Paris: E. Flammarion. 388 pp., 80 fig.

Notes on Qualitative Analysis; for Students of the Rensselaer Polytechnic Institute. By W. P. MASON, 5th ed. 57 pp., tabs. Easton, Pa.: Chemical Publishing Co. Price, 80c.

Text-book of Quantitative Chemical Analysis. By J. C. OLSEN. New York: D. Van Nostrand Co. 3rd ed., rev. 1908. (D 12) c., ill, tabs., 8°. Price, $4.00.

Thermoelemente und Thermosäulen. By DR. FRANZ PETERS. Ihre Herstellung und Anwendung. Halle a. S: Verlag von Wilhelm Knapp. 1908. pp. 180.

Synthèse et constitution des albuminoides. By EMM. POZZI-ESCOT. 110 pp. 1 fr. 50. Lib. Paris: Jules Rousset. 1908.

Some Electro-Chemical Centres. By J. N. Pring. Manchester: Sherratt and Hughes, University Press. 1908. 8°, 136 pp. Price, 1s. 6d.

Préparation mécanique des minerais. By C. Ratel. Paris: 1908. gr. in-8 574 pp av 11 planches et 190 figures. Price, M. 18.80.

Laboratory Notes on Industrial Water Analysis. By Ellen H. Richards. New York: John Wiley & Sons, 1908 (1909). c. 3+49 pp. tabs., 8°, cl. Price, 50c.

Laboratory Guide of Industrial Chemistry. Allen Rogers. New York: D. Van Nostrand Co. c. il. tabs., 8°. Price, $1.50 net.

Laboratory Manual of Qualitative Analysis. By W. Segerblom. London, 1908. 8°. Price, $1.00.

La Chimie dans l'art militaire moderne. By Serrant-Bellenoux. 1 vol. in-8°. 131 pp. 2 fr. 50. Paris: Lib. H. Desforges. 1908.

Story of Iron and Steel. By J. R. Smith. London, 1908. 8°, 206 pp., with figures. Price, 75c.

Factory Glazes for Ceramic Engineers: A West Riding Expert. By E. and F. N. Spon. Ltd., London. Price, 42 s. net.

Practical Metallurgy. By Thomas Turner. London: Charles Griffin & Co., Ltd. 1908.

Cyanide Processes. E. B. Wilson. 4th ed. New York: John Wiley & Sons. London: Chapman and Hall, Ltd. 1908.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

Abstracts of papers read at the Pittsburg meeting Dec. 28 and 29, 1908, in complete form for publication in the annual volume of the Institute.

Modern Electric Pyrometry.

By Edwin F. Northrup.

This paper gives a discussion of the various conditions under which electric pyrometers could be used and the accuracy of temperature measurements which could be obtained from the temperature of liquid air to 1200° C. The resistance thermometer is more accurate and reliable than the thermocouple. Between 1200°–1600° C. the platinum plus 10 per cent. rhodium thermocouple will take its place. The accuracy even at 1200° C. is within 2 to 5 per cent., while ordinary temperatures can be registered to 100th of a degree.

But few chemicals or manufacturing processes are independent of temperature changes which vitally influence the money value of the product. It is impossible to obtain an accurate control of the temperature of the processes without some form of pyrometer or other temperature measuring device. The objection to pyrometers of apparent unreliability is usually due to improper usage in the hands of inexperienced operators, to uses at ranges other than that for which they are intended, or to cheap and unreliable wiring systems. The resistance pyrometer is superior to the thermocouple for temperatures from that of liquid air to 1200° C. because of the greater available energy obtained from a battery.

No fixed design for pyrometers is possible, each manufacturer requiring instruments designed according to his needs. Any number of thermometers may be read by a single indicator at a convenient location or the record of any instrument may be kept on an automatic recorder which is accurate and reliable.

A few of the extensive uses to which pyrometers may be put are air temperatures, lead kettles, steel annealing furnaces, sulphur acid manufacture, etc. The principles and construction of electrical pyrometers is well understood and obtaining successful and accurate results now depend on the intelligence used in their installation and operation.

The Use of Pulverized Fuel for Heating Industrial Furnaces.

By Richard K. Meade, Nazareth, Pa.

This paper discussed the advisability of using pulverized fuel in place of producer gas for heating metallurgical and industrial furnaces. It also called attention to the precautions which are necessary to guard against explosions and fires in the preparation of pulverized fuel. The various forms of dryers used to free coal from moisture, of the mills used to pulverize the fuel, the apparatus employed for injecting the coal into the furnace were described and illustrated with lantern slides. The paper closed with an estimate of the cost of a model fuel plant and some views of particularly up to date installations.

The Examination of Flue Gases in Boiler Tests.

By H. [illegible] Hunicke.

It was shown that the oxygen equivalent, which the authors define as the sum of the volumes of oxygen, carbonic anhydride and carbonic oxide corrected to their respective equivalent volumes of oxygen is a convenient means of studying combustion phenomena. The data of the Fuel Testing Plant of the United States Geological Survey are plotted on a chart and discussed. The author concludes that for the present we cannot hope to gain much more information from the flue gases than that most valuable instrument, the carbonic acid recorder, already reveals.

An Apparatus for Testing Liquefied Ammonia Gas.

By F. W. Frerichs, St. Louis, Mo.

A review was given of the apparatus now in use in the United States and in Europe. It was pointed out that one source of error inherent in some of the apparatus arose from the moisture contained in the atmosphere, which could not be excluded from the sample. The new apparatus excludes this error entirely and its accuracy was demonstrated by repeating the experiments of Lange and Heffter (Chemische Industrie 1898, p. 2) with liquefied ammonia gas of greatest purity and also with mixtures of this ammonia with known quantities of benzole, pyridine, alcohol and water. The liquefied ammonia gas used in these tests had been made from sulphate of ammonium previously purified from all volatile carbon compounds. For this reason it was certain

that no carbon compounds like benzole, pyridine, alcohol, etc., could be present and the amount of water was ascertained (by treatment with metallic sodium and measuring the hydrogen evolved) to be less than 0.002%. The average of the five analyses made in the new apparatus of this ammonia showed it to leave upon evaporation a residue of not more than 0.00175% consisting principally of water, iron oxide and lubricating oil; while Lange and Heffter, using Urbans method, have worked with liquefied ammonia gas leaving upon evaporation 0.2% of a non-volatile residue.

Evaporation test of pure liquefied ammonia gas containing known quantities of benzole, pyridine, ethyl alcohol or water.

Substances present.	Liq NH_3, grams.	Addition, grams.	Addition evaporated by Urban. Per cent.	Addition evaporated by F. F. Per cent.
C_6H_6 and C_5H_5N...	99.0	1.0	00	15
Benzole	98.5	1.5	41	59
Pyridine..........	99.0	1.0	33	24
Ethyl alcohol......	99.0	1.0	20	17
Water	98.9	1.1	17	11
Used ammonia, leaving upon evaporation			0.2	none

The limit of accuracy of testing with the new apparatus has been ascertained to be as follows:

For water 0.002% For alcohol 0.006%
For pyridine 0.009% For benzole 0.110%

PERSONAL NOTES.

On Feb. 13, in the Academy of Music, Philadelphia, the degree of L.L.D. was conferred on Mr. Swank by Temple University. This honor was conferred on Mr. Swank as a recognition of his great service to the business interests of the country and also as a tribute to his literary attainments as shown in his books including "Iron in all Ages," "Notes and Comments" and "Progressive Pennsylvania."

S. B. Sheldon, General Superintendent of the Lackawanna Steel Company, Buffalo, N. Y., has resigned and accepted a position with the Bethlehem Steel Co., Bethlehem, Pa.

Mr. Geo. F. Docons, Assistant General Superintendent, has been appointed General Superintendent, Lackawanna Steel Company.

Mr. Thos. Mathias, Superintendent of rolls, has been appointed Assistant General Superintendent, Lackawanna Steel Company.

Jose Francisco de Navarro, founder of the Atlas Portland Cement Co. at Northampton, died at his home in New York, February 3rd, at the age of 71 years.

"Purification of Ground Waters Containing Iron and Manganese" is the title of a paper by Robert Spurr Weston, who is employed by the Board of Water Commissioners, Reading, Mass. The article is reported in *Engineering Record* of Feb. 3rd, and was read before the meeting of American Society of Civil Engineers at their December meeting.

Mr. G. L. Norris, after a long service with the Standard Steel Works, Burnham, Pa., as chemist and engineer of tests, has resigned to accept the position of engineer of tests with the American Vanadium Company, 324 Frick Building, Pittsburg, Pa., works at Bridgeville, Pa. Mr. Norris in 1890 was First Asst. Chemist, Illinois Steel Company, South Chicago.

INDUSTRIAL AND TRADE NOTES.

The *Daily Consular Report* of January 30, 1909, states that Consul Paul Lang reports from Sherbrooke that asbestos has been discovered near Eastman, Quebec, and that several companies have organized to develop the new mines. The consul continues:

The Orford Mountain Railroad is near these properties, and a spur will be built from the main line to the mills, which are already in course of construction. This discovery is important, as bearing on the extent of the asbestos fields in this province. The mines near Danville, Quebec, some 65 miles from this new find, and at Thetford Mines, Black Lake, and Broughton, Quebec, and several smaller places on the line of the Quebec Central Railway, about 100 miles from Eastman, are now the only producers of this mineral on this continent. [With the exception of a small output in Vermont and a new mine in Georgia.—B. of M.] The development of these new mines will induce more thorough prospecting all over the eastern townships.

Representatives of the Millers' National Federation met in the Auditorium Hotel, Chicago, January 8th, to consider means of obtaining the withdrawal of an order of the Department of Agriculture against the bleaching of flour. It is probable that Secretary Wilson will be asked to lay the matter before a board of referees composed of milling experts for final decision.

It was reported from Bisbee. Ariz., January 4th, that work on the Calumet and Arizona smelters at Douglas was progressing rapidly. The new 500 ton stack was working over time and producing nearly 60 tons a day. All of the old furnaces will be increased and will practically double their present output. The furnaces are now 300 tons capacity but this will be increased to 500 tons.

The production of copper in the United States during 1908, as compiled by L. C. Gaton, of the U. S. Geological Survey, shows a considerable increase over 1907. The increase amounts to about 50,000,000 pounds, or between 5 per cent. and 6 per cent. more than the production of 1907, which was 8,996,491 pounds.

It is reported from Butte, Mont., that although no complaints are made about the Great Falls smelter, the Amalgamated Co. is spending $500,000 there in building a stack and dust chambers, for the purpose of saving flue dust and arsenic, and rendering the sulphur fumes as little harmful as possible. The stack was completed some time ago. It is hoped that it will save flue dust to the value of $180,000 per year. It is 506 feet high and has an outside diameter at the top of 50 feet. The flue dust will be precipitated by means of a new system consisting of a forest of fine wires strung from the ceiling of the dust chamber. There are 1,300,000 of these wires and more than 1000 hoppers have been built to receive the dust. The hoppers discharge automatically into cars which carry the dust direct to the reverberatory furnaces, where it is smelted. The tracks under the great dust chamber resemble a freight-yard.

For eleven months in 1908, Germany imported 147,114 tons of copper and exported 8,034 tons. The consumption was 139,080 tons as against 105,317 tons for the same period in 1907. Of the quantity consumed in 1908, 134,906 tons were imported from the United States.

A new $2,500,000 steel company has been organized for Chicago, with New York and Chicago capital. The plant will be located at Chicago Heights and construction will be commenced during the present month. The company will be known as the Inter Ocean Steel Company and will manufacture steel tires for locomotive wheels, car equipment, rolled steel shells and other circular sections used in mining machinery. It will be independent of the U. S. Steel Corporation. The Board of Directors is composed of: E. C. Converse, president Bankers' Trust Company, New York; W. T. Graham, president American Can Company; Frederick H. Easton, president American Car & Foundry Company; Julian Kennedy, engineer, Pittsburg; John S. Runnells, vice-president Pullman Company, Chicago; Arthur Meeker, Armour & Co., Chicago; Mason B. Starring, president Northwestern Elevated Railway, Chicago; W. V. D. Wright and W. L. Jacoby, respectively treasurer and president of the new company.

Julian Kennedy, for many years general manager of the Carnegie Steel Company at Homestead, Pa., and an engineer famous the world over, is designing the plant. There will be open-hearth furnaces and rolling mills included in the equipment.

The second case against the Standard Oil Company of Indiana was brought to trial before Judge A. V. Anderson at Chicago, on February 23. This is the world famous case, in which at the conclusion of the first trial, a $29,000,000 fine was assessed by Judge K. M. Landis.

The work of the U. S. Geological Survey, as shown by its 1908 report, shows it to be of the most diverse character, ranging from that of the explorer and geographer making surveys in interior Alaska to that of the mining engineer, investigating gas and coal dust explosions and mine explosives, together with the considerable work of a purely geological nature. The appropriations for the year amounted to $1,782,770 and more than 150 parties were in the field.

The metal output of Utah during 1908 had a value of not much more than half that of 1907. Several causes contributed to this result. While the production held up well, prices fell off to a large extent, and further difficulty was caused by the closing of smelters by court order on account of damage by smelter fumes to agricultural products and stock. The copper production for 1908 was 74,000,000 lbs. as against 98,800,000 lbs. in 1907; the price for 1908 was 13 1/8 cents per lb. as against 20 cents in 1907. The total value for 1908 was slightly under $10,000,000 as against $19,760,000 in 1907. Gold production dropped from 750,802 ounces, valued at $11,416,040 in 1907, to 250,000, ounces valued at less than $5,000,000 in 1908. The silver produced amounted to $17,204,100 ounces in 1907, which was valued at $11,354,651; whereas in 1908 the production was about 10,000,000 ounces, of a total value of less than $5,000,000. The lead production dropped from 142,176,000 lbs. in 1907 to 103,000,000 lbs. in 1908, and the value from $7,108,800 to about $3,350,000.

On January 25, there was formed at the Waldorf Astoria in New York an organization of manufacturers of foods, to oppose the use of chemical preservatives and chemicals in foods. The organization is called the American Association for the Promotion of Purity in Food Products. Resolutions were adopted, stating that since "certain reactionary interests" opposed to the enactment of a national pure food law are now opposing its enforcement and by concerted action have been able to nullify in great measure some of the important provisions of the law, the members will give their moral and financial support and their undivided influence toward upholding "the proper and legitimate efforts of the regularly constituted officials charged with the administration of all laws looking to the elevation of the food-producing interests of the country.

The total copper production in the United States during 1908 amounted to 868,996,491 lbs., an increase of 50,000,000 over 1907. Imports decreased about 13 per cent. and exports increased about 30 per cent.

The output of petroleum in the state of California for 1908 amounted to 50,000,000 barrels, The Kern river district produced 13,000,000 barrels; Coalings district 12,000,000 barrels; Santa Barbara produced 9,000,000 barrels; Fullerton 4,000,000 and Salt Lake 4,000,000. Other districts run as follows: McKittrick, 3,500,000; Sunset, 1,500,000; Whittier, 750,000; Los Angeles city, 475,000; Midway, 400,000, and Ventura, 300,000.

The total production of bituminous coal in the United States amounted to 330,000,000 tons in 1908 as against 400,000,000 in 1907.

The report of the Food Referee Board, consisting of Dr. Ira Remsen, president of Johns Hopkins University; Russel H. Chittenden, director of the Sheffield Science School of Yale University; John H. Long, professor of chemistry, medical school, North Western University; C. A. Herter, professor of physiological chemistry, College of Physicians and Surgeons, New York, and Alonze E. Taylor, professor of pathology, University of California, and appointed last March by the Secretary of Agriculture at the suggestion of President Roosevelt, was handed to the Secretary January 23. The questions submitted by the President to the Board were as follows: 1. Does a food to which there has been added benzoic acid or any of its salts, contain any added poisonous or other added delectorious ingredient which may render the said food injurious to health? In large quantities? In small quantities?

2. If benzoic acid or any of its salts be mixed or packed with a food is the quality or strength of said food thereby reduced, lowered, or injuriously affected? In large quantities? In small quantities?

"To make this experimental inquiry as thorough as possible," says the report of the board, "and to minimize the personal equation, three independent investigations have

been carried out: One at the medical school of Northwestern University in Chicago, a second at the private laboratory of Christian A. Herter of Columbia University, New York, and the third at the Sheffield Scientific School of Yale University.

"The same general plan of procedure was followed in all three experiments. A certain number of healthy young men were selected as subjects and during a period of four months these men under definite conditions of diet, etc., with and without sodium benzoate, were subjected to thorough clinical and medical observation, while the daily food and the excretions were carefully analyzed and otherwise studied and comparison made on clinical, chemical bacteriological and other data collected. In this manner material has been brought together which makes possible conclusions regarding the effect of small and large doses of sodium benzoate upon the human system."

The board says that the fact should be emphasized that the results obtained from the three separate investigations are in close agreement in essential features. The main general conclusions reached by the board are:

First—Sodium benzoate in small doses (under 0.5 gram per day) mixed with food is not deleterious or poison, and is not injurious to health.

Second—Sodium benzoate in large doses (up to 4 grams per day) mixed with the food has not been found to exert any deleterious effect on the health nor to act as a poison in the general acceptation of the term. In some directions there were slight modifications in certain physiological processes, the exact signification of which modifications is not known.

Third—The admixture of sodium benzoate with food in small or large doses has not been found to injuriously affect or impair the quality or nutritive value of such food.

Dr. Wiley as the result of his experiments says[1] that "from a careful study of the data in individual cases and of the summaries of the results, it is evident that the administration of benzoic acid, either as such or in the form of benzoate of soda, is highly objectionable and produces a very serious disturbance of the metabolic functions, attended with injury to digestion and health."

"These injurious effects," says Dr. Wiley, "are evident in the medical and clinical data which show grave disturbances of digestion attended by phenomena which are clearly indicative of irritation, naseau, headache and in a few cases vomiting."

In concluding, Dr. Wiley said: "Coming to the final consideration of all these different phases of the subject, there is only one conclusion to be drawn from the data which have been presented and that is in the interests of health both benzoic acid and benzoate of soda should be excluded from food products. This conclusion is reached independently of any consideration of the conditions which it is alleged surround the processes of manufacture and which result in the demands of manufacturers to be allowed to continue the use of these substances. This is a subject which must be discussed from an entirely different point of view and has no bearing whatever upon the general conclusions which have been reached, namely, that both benzoic acid and benzoate of soda are bodies which when added to foods are injurious to health."

[1] Bull. 84, Part 3, Bur. Chemistry.

It is reported that the experiments thus far made in the testing laboratory of the U. S. Geological Survey at Pittsburg, have shown that mine explosions can be minimized or prevented by forcing steam through the air currents produced by the ventilating fan of the mine. A miniature mine was constructed at the testing plant, and the conditions inside were made as nearly as possible like those in a real mine with a quantity of dust in it. In the presence of mine superintendents, foremen and engineers, steam was turned into the dust-laden air of the miniature mine, and it was found impossible to cause an explosion. Cold dry air was then forced into the mine, and the explosion took place almost instantly. The same experiments were tried repeatedly, with the same results.

This use of exhaust steam was suggested two years ago and put into effect by H. A. Kuhn, president of the Pittsburgh & Westmoreland Coal Co. Since resorting to this measure as a precaution explosions have been unknown in the Pittsburgh–Westmoreland mines.

Further tests by the government experts are to be made, with the idea of trying out the theory in every known form.

On January 22nd President Roosevelt sent to Congress a special message transmitting the report of the National Conservation Commission, which was appointed by him in June, 1908, to inquire into and advise him as to the condition of the country's natural resources. The report discusses lands, forests and waters. "The facts set forth in this report constitute an imperative call to action," says the President in his letter of transmittal. "The situation they disclose, demands that we, neglecting for a time, if need be, smaller and less vital questions, shall concentrate an effective part of our attention upon the great material foundations of national existence, progress and prosperity."

He discusses the various recommendations approvingly, and concludes with the suggestion that an appropriation of at least $50,000 be made to maintain a national conservation commission. "This is a very small sum," he says. "I know of no other way in which the appropriation of so small a sum would result in so large a benefit to the whole nation."

On Jan. 18th, the Supreme Court affirmed the judgment of the Texas courts imposing a fine aggregating $1,623,900 on the Waters-Pierce Oil Co. for violating the anti-trust laws of that state.

The National Tube Co. of Lorain, Ohio, have completed their new open-hearth plant of seven furnaces.

The new rail mill of the Indiana Steel Co. at Gary was tried out Jan. 17th, and rails were produced from steel sent from the Illinois Steel Co. at South Chicago.

The Illinois Steel Co.'s plant at South Chicago has nearly resumed full capacity. Blast furnace No. 10, idle since Nov., 1907, was blown in Jan. 31st. Blast furnace E, idle since Jan., 1908, was blown in Feb. 8th. The steel mill and rail mill, idle since Dec. 31st, 1908, were started again

Feb. 8th. Cement plant No. 2, located at South Chicago, idle since Sept. 1908, started producing again Feb. 1st.

It is reported that a new $200,000,000 organization, the North American Portland Cement Company, which includes plants with an output of nearly 40,000,000 barrels, has been formed.

A bill was introduced in the House of Representatives, sixtieth congress, first session, by Mr. Currier, No. H. R. 21455, entitled "A Bill to Establish a United States Court of Patent Appeals and for Other Purposes." If this bill is passed, it will do away with the grievous conditions that exist now in patent litigations before the circuit courts (see address by Louis C. Raegener in this number). The bill has been favorably reported upon, as will be seen by reading the arguments before the Committee on Patents of the House of Representatives, March 18th, 1908, number H.R. 14047. All chemists, all engineers, all inventors, as well as the public at large are interested in this subject and it is very desirable that the bill should pass. The members of the Committees of the House and of the Senate who will have the bill under consideration are as follows:

Committee on Judiciary of the House of Representatives: John J. Jenkins, of Wisconsin, *Chairman*; De Alva S. Alexander, of New York; Charles Q. Tirrell, of Massachusetts; John H. Foster, of Indiana; Reuben O. Moon, of Pennsylvania; George R. Malby, of New York; David A. DeArmond, of Missouri; Robert L. Henry, of Texas; Charles C. Reid, of Arkansas; Richard Wayne Parker, of New Jersey; Charles E. Littlefield, of Maine; John A. Sterling, of Illinois; Henry T. Bannon, of Ohio; Garrit J. Diekema, of Michigan; Henry S. Caulfield, of Missouri; Henry D. Clayton, of Alabama; William G. Brantly, of Georgia; Edwin Y. Webb, of North Carolina.

Senate Committee on Patents: Hon. Reed Smoot, of Utah; William H. Milton, of Florida; Frank B. Brandegee, of Connecticut; Frank B. Gary, of South Carolina; Alfred B. Kittridge, of South Dakota; Murphy J. Foster, of Louisiana; Moses E. Clapp, of Minnesota.

According to the press reports of January 26th, Federal Judge Hunt has declined to issue an injunction against the Washoe smelter of the Anaconda Copper Mining Co. at Anaconda, Mont. The complaint of the plaintiff, who in reality represents the Deer Lodge Valley Association. is not dismissed, but the court desires additional information before final disposition of the case is made. February 15th was named by Judge Hunt as the time for the hearing of new testimony, and E. P. Mathewson, manager of the smelter, and others were ordered to appear in court at that time.

This case is of particular interest as it represents the largest suit growing out of the alleged damage to vegetation and stock by smelter smoke, and is the first suit in the west that has not been decided in favor of the complainants. Had the injunction been granted the paralysis of the mining and smelting industries of the Butte district—as well as of many other industries directly or indirectly dependent upon them—would have been assured.

The H. C. Frick Coke Co., the coking company of the United States Steel Corporation, has decided to abandon work on additional coke ovens in Pennsylvania, which were to be built at a cost of $3,000,000, and in their stead construct an enormous coking by-product plant at Gary, Ind. It will take the place of 700 ovens, which were to have been built at Filbert, 500 at Ralph, and 500 at Sarah, Pa. In the meantime the company is opening new mines to supply the ovens with coal.

It was the intention of the Steel Corporation to build more beehive ovens in the Connellsville region in Pennsylvania, but it has decided to build an extensive series of by-product ovens instead, thus saving all the gas now wasted in coking coal, besides saving the ammonia and other coal tar products.

Platinum Mining in Russia.—Consul-General Hunter Sharp, of Moscow, advises that owing to the depression in the platinum-mining industry in Russia, the platinum miners have applied to the Government asking that the industry be upheld until it is definitely decided whether the mining of platinum is to be made a monopoly of the Russian Government. The platinum miners have petitioned the Government for temporary assistance; that is, to permit the Russian Imperial Bank .to grant loans on platinum ore containing 83 per cent. of pure platinum, at the valuation of 16,000 rubles per pood ($8,240 per 36 pounds), with interest at the rate of 5 per cent. per annum.—*U. S. Consular Report*, Jan. 26, 1909.

Nitrate of Soda Supply.—According to Consul Rea Hanna, of Iquique, the Delegacion Fiscal, or Official Board of Engineers, states the following in its annual report to the Government of Chile:

It is the current opinion in Europe and the United States that our nitrate deposits will be exhausted after a maximum period of forty years, and so widely spread is this error that the subject has been considered in the annual report of the Secretary of Agriculture presented to the Congress of the United States. Perhaps the data submitted by the delegation in former years caused the lack of confidence, but the data then given were the results of this office up to that time, and at present the aspect is entirely different. The experience of the last ten years has shown that the former figures do not nearly approximate the actual conditions. The report of 1896 gave the following figures in Spanish quintals of 101.61 pounds, which were confirmed later in 1906:

	Quintals.
Tarapaca: Nitrate of soda contained in the fields according to the private and official measurements and estimates	573,000,000
Toco: Nitrate of soda contained in the fields according to the private and official measurements and estimates..	225,000,000
Antofagasta, Aguas Blancas, and Taltal: Private measurements and estimates only (not official)............	305,000,000
Amount calculated in unworked official fields...........	500,000,000
Total possible production in nitrate zone	1,603,000,000

With a probable annual exportation of 35,000,000 quintals this estimate gave, in 1899, enough nitrate to last forty-six years before being exhausted.

After a detailed discussion of the shortcomings of the former estimates and the increasing importance of the Anto-

fagasta Pampa on account of recent developments the delegation reports:

We have then the following total:

	Quintals.
Tarapaca	740,000,000
Antofagasta	4,103,000,000
Total	4,843,000,000

FUTURE SUPPLY OF NITRATE OF SODA IN CHILE.

There are then undeniably 4,843,000,000 Spanish quintals of nitrate of soda in sight, which by the methods in use at the present time may be produced from the lands measured and estimated in the nitrate region. With an annual exportation of 35,000,000 quintals, which is more than that exported in 1907, there is sufficient to satisfy the entire consumption of the world for one hundred and thirty years.

[The complete official report from which the foregoing was taken may be seen at the Bureau of Manufactures.]—*U. S. Consular Report*, Feb. 10, 1909.

Rubber Production, Mexico.—Consul Charles M. Freeman, of Durango, sends the following in response to an inquiry from Boston as to the opportunities in that Mexican State for an American with a few thousand dollars to engage in rubber production, particularly from the palo colorado tree:

The first absolute necessity for a person contemplating the rubber or any other business in Mexico is a knowledge of the Spanish language. While there are many in Mexico engaged in business who have no knowledge of Spanish, they are handicapped in their operations and, being dependent on an interpreter, their ultimate success is doubtful. Only one rubber-producing plant in northern Mexico, the guayule, has been developed into a commercial success. This and all others grow far from civilization, in localities where the English language is never spoken. The guayule rubber ground is well covered by companies capitalized to the extent of millions of dollars. There is no opportunity for a person of limited means to compete in the guayule region.

The production of rubber from palo colorado and other mild rubber-producing plants, aside from guayule, is in an experimental stage. The exploiters feel certain that they have a good thing, but as they are not getting out any gum it is not possible to give positive statements covering all of the business. From the number of inquiries received at the consulate from consumers of raw rubber it would appear that the market is not only ready, but waiting for the gum of the palo colorado. Further developments are awaiting the verdict of chemists who are working on the raw material to determine exactly its adaptability to certain uses and its commercial value. Should these points be settled satisfactorily, an extensive business in the gum of the palo colorado may be expected.

POSSIBLE RESULTS FROM PALO COLORADO.

The tree grows at least four days' journey from this city, in the Sierra Madre Mountains, to which point all material must be packed on mules or burros, and from which gum must be freighted in the same manner.

Approximately, the cost of production in American currency per kilo (2.2 pounds) is as follows: Employment of natives for the purpose of tapping the trees and delivering the gum at some central station, 12 1/2 cents; freight from central station to railroad, some three or four days' journey, 2 1/2 cents; freight from Mexican railroad station to market in the United States, 5 cents; total, 20 cents per kilo or about 10 cents per pound.

The foregoing does not include the proportionate share to be placed on each pound of gum produced for the interest on the capital invested in leasing or buying land on which the tree grows, nor the proportionate share for management, high-priced labor, government taxes, and other necessary expenses.

Attention is called to the difference in cost between laborers and management. Good laborers can be hired for $10 a month, while a person capable of managing labor, who can speak both English and Spanish, can not be had under $100 American currency.

Guayule sells in the markets of the United States for about 25 cents American currency per pound, and is said to contain 10 per cent. of pure rubber. The palo colorado at the same price should be a good investment, provided the chemists' analysis is favorable. In fact, if, as the exploiters claim, the palo colorado contains over 30 per cent. of pure rubber, then the price should be much greater for the palo colorado than for guayule.

The first work in the rubber business is to locate the trees and to buy the land or lease the privilege of tapping the trees. To do this work is not so simple a matter as in the United States and one finds many obstacles to be overcome. The most satisfactory results will be obtained by employing some person acquainted with Mexican laws and localities to act, under supervision, as agent in this matter. There are reliable persons who, to a certain extent, make that their business.

There seem to be possibilities of success with the palo colorado. If the tree is to be found in sufficient numbers, and if the chemists' report should be favorable, the business will be an assured success. If a success, the first to put the gum on the market will get the profits. However, in the light of present developments, the business is very much of a venture and likely to prove for a person not fully acquainted with all that has been accomplished an unprofitable one. It is estimated that it would take $5,000, possibly twice that amount, before a pound could be marketed.

Barytes in Germany.—Consul-General Robert P. Skinner, of Hamburg, writes that he has been asked to supply information respecting the cost of barytes, which in hearings before Congress was said to be worth $2.78 per ton at the foreign seaports in 1885. Mr. Skinner reports:

This material is used almost exclusively in the paint trade, being ground and mixed with white paint to give it body. The best grades, from the Harz and Thuringian mountains, are naturally white, and can be used without first being bleached. To some extent these grades are utilized in the porcelain and white-glass industries. The cheaper grades of barytes come from the Rhine, are shipped in crude form, and these, both hard and soft, are exported to the United States, where they are treated chemically and made white. Barytes from the Rhine and from Newfoundland contain 96 per cent. of barium sulphate.

The exporting points for barytes in Europe are Rotter-

dam, Antwerp, and Hamburg. There are many mining firms in the business, and they have formed a pool to maintain prices and apportion the tonnage. It is said that exporters get the same quotations from all producers, who turn back orders when their quota is reached.

Hamburg exporters invariably buy on terms delivered at seaboard. The prices now (December 1) are from $5.47 to $5.71 per ton. The ocean freight from seaboard to New York runs from $1.70 to $2.19 per ton. The German rate from mine to seaboard, shipments being made in large barges, is from $1.19 to $1.42 per ton. This would bring the present price at the mine from $4.05 to $4.52. Since the pooling arrangement referred to prices have been advanced from 50 to 75 cents per ton, although labor cost, it is stated, has also advanced.—*U. S. Consular Report*, Feb. 1, 1909.

Australia's Mineral Wealth.—Consul-General John P. Bray writes from Sydney that the mineral output of Australia up to the end of 1907 reached $3,350,969,703, and that as there was a further production in 1908 amounting to probably no less than $97,330,000, the total is now about three and a half billion dollars, of which fully two and a half billion dollars represent gold. Mr. Bray continues:

For a long time after the gold discoveries in 1851 that metal, in the main, represented Australia's mineral output, but after the total of $62,841,114 was reached in 1856 there was a steady decline until, in 1886, the gold output was only $21,548,862. With the opening of the Western Australian gold fields this position was materially altered and the 1856 production was exceeded in 1899. The maximum output was reached in 1903. The following table gives the production of metals and minerals since 1895:

Year.	Gold.	Silver-lead	Copper
1895..........	$37,510,982	$9,285,282	$1,951,466
1896..........	38,625,410	9,966,592	2,155,859
1897..........	47,492,173	9,392,345	4,199,789
1898..........	56,991,581	9,713,534	4,433,381
1899..........	71,347,756	12,044,587	10,097,987
1900..........	66,680,783	13,981,454	8,662,370
1901..........	69,055,635	10,433,776	10,219,650
1902..........	72,106,930	9,416,677	7,703,669
1903..........	79,294,751	9,003,025	8,263,317
1904..........	77,576,876	12,584,769	7,922,662
1905..........	75,722,740	13,927,923	11,071,287
1906..........	71,206,628	17,636,196	16,278,442
1907..........	65,751,281	22,969,880	17,096,014

Year.	Tin.	Coal.	Other.
1895..........	$1,153,360	$6,618,440	$885,703
1896..........	1,377,219	6,379,981	656,977
1897..........	978,166	7,275,417	1,250,690
1898..........	997,632	7,528,475	1,338,287
1899..........	2,311,587	8,068,657	4,170,590
1900..........	2,219,124	9,835,196	2,769,038
1901..........	1,121,794	12,764,829	2,550,046
1902..........	2,087,728	12,896,225	2,919,900
1903..........	3,357,885	12,808,628	3,017,230
1904..........	4,014,862	11,334,078	3,946,731
1905..........	4,995,699	11,377,877	4,297,119
1906..........	71,206,628	12,993,555	4,199,789
1907..........	7,309,483	16,074,049	8,842,430

U. S. Consular Report, Jan. 30, 1909.

Peanut-oil Industry.—Consul-General Robert P. Skinner, of Hamburg, after referring to his former reports from France on the peanut-oil industry and expressing the belief that interest in this subject will not subside until mills have been erected in the United States and a peanut crop assured large enough to supply the demand, gives the following additional information:

The Department of Agriculture at Washington is now at work on this subject and is experimenting with African seed nuts which were shipped from this consulate to the United States some months ago. At the present time, and probably contrary to the American impression, the annual crop of groundnuts is not always sufficient to supply the cravings of the domestic appetite. It frequently happens that the west coast of Africa is called upon to make good this shortage, although there is no reason whatever why a forage plant so useful as the peanut, and a kernel so valuable, should not be produced in the United States in practically unlimited quantities. It happens also, that an American oil industry is rendered difficult of establishment, not only because of the uncertainty of the crop, but because the American nut is less rich in oil than the African. The Department of Agriculture is now studying this phase of the matter, hoping, no doubt, to develop an edible nut which will be as palatable as the varieties now on the market, and as rich in oil as the African kernels.

The first step to be taken, naturally, in building up an American peanut-oil trade is to increase the crop of peanuts. In 1900, according to the census returns, the American crop was 11,964,109 bushels, or roundly, 326,294 tons. As Marseille alone imports upward of 200,000 tons of these nuts for French oil mills, it can be judged that the total American crop is a comparatively small affair. Hamburg has come into the importing market more recently, receiving only 11,903 tons in 1907. London is also an importing center. Marseille, therefore, retains its preeminence as the European oil center, and American investigators can learn more of interest and importance there than elsewhere.

West African nuts (Ruffisque, Cayor, Sine, Gambia, Bas de Cote) are usually exported in the shell, and produce edible oil of the highest grade. Other kernels are usually, but not always, received decorticated. The percentages in oil of the best-known grades run as follows: Senegal 51, East African 49, American 42, Bombay 44, and Madras 43.

The oil is obtained by pressure, the first application being while the material is cold, or to be more exact, very slightly heated, and the second and third pressures hot Upon reaching the mill the nuts are first winnowed and then shelled. The kernels are next broken into large pieces and at the same time freed from the red skin to some extent, and from foreign matter completely. The material is then reduced to a fine flour, placed in bags, and pressed cold during one hour. The cake, after the first pressing, is broken, heated to 70 degrees C., and pressed a second and third time. The resulting products per hundredweight of decorticated nuts run in percentages about as follows: First-class oil, 31.5; second-class oil, 10; oil cake, 54.5; losses, etc., 4.

In Europe a first-class peanut oil is the most highly esteemed of vegetable oils after olive oil. It is also used in the manufacture of butter substitutes. The low-grade oils are taken up by the soap trade.

Raw material enters France free of duty, but the oils are dutiable at the rate of 6 francs ($1.16) per 100 kilos (220 pounds) It would be impossible, probably, for peanut

oil of foreign manufacture to compete in the Marseille market with the domestic article.

The prices per 100 kilos at Marseille, on November 20, 1908, were as follows: Edible oil, $13.51–15.44; soap oil, $11.97; Bombay peanuts, shelled, $5.84; Mozambique peanuts, shelled, $7.14; Ruffisque nuts, in the shell, $4.58; Bas de Cote, $5.35; peanut cake, $3.13. During ten months of 1908 Marseille received 92,707 tons of shelled peanuts and 94,737 tons in the shell.

German manufacturers press peanuts three times, twice for edible oil and once for soap oil. Ruffisque kernels are chiefly utilized. It would cost in this country about $23,800 to erect a mill of 10 tons' capacity and about $83,300 for one of 50 tons' capacity, exclusive of the cost of real property and buildings.

Prices to-day (November 27, 1908) per 220 pounds in Hamburg for peanuts in the shell are $5.24; shelled, $5.71; oil from $14.76 to $21.42. German peanut cake commands from $35.70 to $38.08 per 2,204.6 pounds. The duty on peanuts in Germany is 2 marks ($0.476) per 220 pounds; that on oil is 10 marks ($2.38) per 220 pounds.

[Consul-General Skinner appends a list of the best-known firms in France and in Germany manufacturing oil presses, which is placed in the files of the Bureau of Manufactures.]

U. S. Consular Report, Jan. 23, 1909.

Rubber-tanned Leather.—A British publication states that a new syndicate has established a factory in London and is placing upon the market a new form of leather, for which it is claimed there is a big future, and which it thus describes:

The leather is submitted to a tanning process of the chrome variety, which preserves it; rubber solution is then worked into the interstices, rendering the hide thoroughly waterproof. The elasticity of the rubber permits of perfect flexibility and extraordinary toughness of some of the skins, especially of rabbit, goat, and sheep skins. It is impossible to forecast the many uses for which this process may be available. Tests have been made for motor tires, soles for boots and shoe, pump washers, machine belting, miner's boots, etc., and it is probable that the multitude of articles that can be made of rubberized leather will, in time, create a further demand for rubber. This new material, it is thought, may also prove useful for motor and cycle tires, as it is almost impossible to puncture it, while it is said to be much more resilient and waterproof than ordinary leather.—

U. S. Consular Report, Jan. 23, 1909.

The Universal Portland Cement Co. is about to start construction on an addition to Plant No. 5 at Universal, Pa.

This plant at present has an output of 4,500 barrels per day. When the new addition is completed, which will be about January, 1910, the total output of this plant will be 10,000 barrels per day or 3,000,000 barrels per year. This will give the Company a total production of 23,000 barrels per day or 8,000,000 barrels per year.

OFFICIAL REGULATIONS AND RULINGS.

Food Inspection Decision, 103.

The Labeling of Turpentine. The Department has received a number of letters with reference to the proper labeling of the product generally known as "wood turpentine," etc., obtained by steam distilling or destructively distilling woods. Food Inspection Decision 58 recognizes that—

Products used in the arts and for technical purposes are not subject to the Food and Drugs Act * * * when plainly marked so as to indicate that they are not to be employed for food or medicinal purposes.

It is held, therefore, that when wood turpentine is labeled "Not for Medicinal Use," etc., it is not subject to the food and drugs act. When not so labeled it is in violation of section 7 of the food and drugs act unless labeled "wood" or "stump" turpentine. Articles labeled "turpentine," "spirits of turpentine," or "gum terpentine," etc., must comply with pharmacopoeial requirements; that is, they must be light oils of certain properties made by distilling the oleoresin of various species of Pinus. The word "wood" or "stump" should be in the same type and on the same background as the word "turpentine," thus being given equal prominence.

H. W. Wiley,
F. L. Dunlap,
Geo. P. McCabe,
Board of Food and Drug Inspection.

Approved:
James Wilson,
Secretary of Agriculture,
Washington, D. C., *January 22, 1909.*

Under date of January 30, the Board of Food and Drug Inspection has issued a notice of judgment No. 36, Food and Drugs Act, Misbranding of Canned Apples and Blackberries. Under the same date judgment No. 37, Food and Drugs Act, Adulteration of Milk (Water).

Treasury Department, *January 4, 1909.*

(T. D. 29455) *Casein.*—Decision of the United States court of appeals, second circuit (suit 4586; T. D. 29374), United States *v.* W. M. Brownell, acquiesced in.

Treasury Department, *January 8, 1909.*

(T. D. 29461) *Drawback on lubricating oils.*—Drawback on lubricating oils manufactured by the Swan & French Company, of New York City, wholly or in part from imported sperm oil, Russian oil, and Japan oil.—T. D. 17355 of August 1, 1896, extended.

(T. D. 1449). *Method of sampling butter.*—Instructions to internal-revenue officers to discontinue use of butter "trier" in taking samples and describing new method to be used in lieu thereof as follows:

Treasury Department,
Office of Commissioner of Internal Revenue,
Washington, D. C., January 2, 1909.

To collectors and other internal-revenue officers and employees:

The act of Congress approved May 9, 1902, imposes an internal-revenue tax of 10 cents per pound on adulterated butter, as described in the act, and special taxes on any

person engaged in the business of manufacturing adulterated butter or in the sale of the same.

The enforcement of this law necessitates the examination of the product found on the market or in storage by revenue officers, who are required to procure samples from the packages so found and submit the same for chemical analysis, by which process it is determined whether any chemicals have been used or any substances foreign to genuine butter have been added, or any process of manipulation has been resorted to with the effect of causing the absorption of an abnormal quantity of water, milk, or cream. Upon the results of these analyses it is determined what butter is subject to the tax herein referred to.

Heretofore, while acting under instructions of this office, care has been taken by field officers to obtain truly representative samples of the contents of the tub or package of butter without particular reference to the method of taking the samples, and complaints have reached this office concerning all these methods, more especially where a "butter trier" has been used. It is claimed that this is especially objectionable for the reason that it disfigures the surface of the contents of the package and interferes with the division of the same into prints. Obtaining the samples from the top, bottom, or sides of the package by means of a spoon or other instrument has been criticized, as not giving representative samples of the contents of the tubs.

Hereafter, in procuring these samples, the use of a "butter trier" will be entirely abandoned. The quantity required from each package will be obtained from the top and bottom or sides of the butter contained in the tubs by cutting a V or wedge shaped strip about 2 inches wide, 1½ inches deep, and of sufficient length to make up the required weight of the sample, which must be approximately 1 pound. This can be accomplished by removing the butter from the tub. A V-shaped strip of this character should be taken from each opposite sides of the package of butter, or from both the top and the bottom of same, but it is regarded as sufficient if two such strips are obtained—that is, from the top and bottom in one case and from the two sides in the other instance.

Butter put up in prints will be sampled by taking a 1-pound print from the box or other container.

All officers and employees engaged in securing samples of butter for investigation are admonished to perform this duty with as little trouble and friction as possible, leaving the packages sampled as nearly in their normal condition as may be practicable.

Any labor required in the handling of packages to be sampled will be performed by the officers, or, if assistance is necessary, by persons employed for that work by the officers in charge of the investigation. The business of merchants or of storage houses should be interfered with as little as possible by officers while in discharge of these duties. In return, it is assumed that the owners of butter will interpose no unreasonable obstacle in the way of officers who seek only to carry out their instructions.

Great care must be exercised in the packing, sealing, labeling, and shipping of samples of butter, following existing instructions as contained in circulars now in force.

JOHN G. CAPERS, *Commissioner.*

TREASURY DEPARTMENT,
January 9, 1909.

(T. D. 29463). *Drawback on zinc shavings.*—Drawback on zinc shavings manufactured by F. W. Braun, of Los Angeles, Cal., from imported zinc in sheets.

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(T. D. 1450). Denatured alcohol produced in and imported from Porto Rico is subject to same tax as alcohol not denatured.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington D. C., January 11, 1909.

SIR: This office is in receipt of your letter of the 9th instant, relative to the manufacture and exportation of the United States of denatured alcohol produced in Porto Rico.

In reply, you are informed that the law authorizing the withdrawal of distilled spirits from bonded warehouse, free of tax for denaturation in the United States, does not apply to Porto Rico, and that importations of denatured alcohol from Porto Rico would be subject to the same tax as the alcohol not denatured.

Respectfully,
J. C. WHEELER,
Deputy Commissioner.

Mr. ——— ———, *Arecibo, P. R.*

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(T. D. 29471). January 14, 1909.—Drawback on Babbitt metal manufactured by the Frictionless Metal Company at its factories at Chattanooga, Tenn., and Richmond, Va., with the use of imported lead and antimony.—T. D. 22963 of April 10, 1901, extended.

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(T. D. 29497—G. A. 6857). U. S. General Appraisers, New York, January 26, 1909.

COLOR—OXIDE OF IRON—LEVIGATED IRON ORE.

Oxide of iron, or hematite iron ore, which is in a powdered state resulting from a process of grinding and levigation, and which is used in the manufacture of paint and in coloring leather board, etc., is dutiable under paragraph 58, tariff act of 1897, relating to colors and pigments, rather than under paragraph 121 as iron ore.—Hill *v.* Francklyn (162 Fed. Rep., 880; T. D. 29074) distinguished.

(T. D. 1453). Adulterated butter.—Revenue officers are enjoined to show utmost consideration for the rights of legitimate business in investigating questions of liability under the act of May 9, 1902.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., January 16, 1909.

To collectors and other internal revenue officers:

My attention has been called to an article in a recent issue of a trade journal relative to the methods pursued by revenue officers in taking samples of suspected butter, and holding up various lots of butter in stores and warehouses.

The article in question cites various instances of butter being held under detention or suspicion for an unreasonable length of time before being released as normal, or seized as adulterated. and is illustrated with a cut made from a photo-

graph of certain tubes released after examination, showing wholly unnecessary mutilation as a result of the methods used in the taking of samples.

The article is doubtless exaggerated, but contains enough truth, judging from certain instances which have come to my notice, to warrant me in again calling attention of all revenue officers to the necessity of using the utmost care and consideration for the rights of legitimate business in making investigations of this character.

Where the field force have facilities for making such tests preliminary tests of suspected butter should be made, and samples showing 15½ per cent. or more of moisture should be at once forwarded to this office, and all tubs from which the samples were taken showing less than that per cent. should be promptly relieved from suspicion, only the tubs showing 15½ per cent. or more being detained to await the results of the official analysis, which will be forwarded with all possible dispatch.

Should the official chemist's report show that any of the detained tubs of butter contain butter of less than 16 per cent. moisture, such tubs should be promptly released and formal seizure made of the tubs found by tests made in the laboratory here to contain 16 per cent. or more of moisture.

The two principal grievances complained of are the injury to the appearance of the packages through the taking of samples and the delay in determining the classification of the suspected article, and it is believed that a careful compliance with T. D. 1449 will minimize the first, and all officers are enjoined to use the utmost effort to avoid the second.

JOHN G. CAPERS,
Commissioner.

(T. D. 29499) *Fire brick.*—UNITED STATES *v.* BEHREND.—UNITED STATES *v.* WING.—U. S. Circuit Court of Appeals, Second Circuit. January 12, 1909. Nos. 90 and 91 (suits 4304 and 4585).

1. FIRE BRICK—RETORT SETTINGS—SIMILITUDE.

Retort settings more than 10 pounds in weight are dutiable by similitude as "fire-brick weighing not more than ten pounds each," under paragraph 87, tariff act of 1897.

2. SAME—MINERAL SUBSTANCES—SUSCEPTIBILITY TO DECORATION.

Fire brick, which can be but never are decorated, are not susceptible of decoration so as to be covered by paragraph 97, tariff act of 1897, which through relating to articles composed of earthy or mineral substances, is limited to such as are susceptible of decoration.

3. SIMILITUDE—POINTS OF RESEMBLANCE—IDENTITY.

Retort settings more than 10 pounds in weight resemble fire brick weighing not more than 10 pounds, in material, quality, texture, and use, within the meaning of the similitude clause in section 7, tariff act of 1897. Identity ordinarily would exclude all question of similarity, but not here, because of the distinction in weight.

4. SIMILITUDE TESTS OF RESEMBLANCE—INCONGRUITY OF ASSESSMENT.

The amount of duty is not one of the test prescribed for the application of the similitude clause in section 7, tariff act of 1897. If incongruity results, the inference is not that the tests should be abandoned, but the Congress failed to express its intention

NOYES, Circuit Judge, dissents.

APPEALS from the circuit court of the United States for the southern district of New York.

[Decision adverse to the Government].

For decision below see T. D. 28718, in which the circuit court, on the authority of Wing *v.* United States (119 Fed. Rep., 479), affirmed decisions of the Board of United States General Appraisers, which are reported as G. A. 6382 (T. D. 27422) and Abstract 13038 (T. D. 27649), and which sustained protests of Fred Behrend and Wing & Evans against the assessment of duty by the collector of customs at the port of New York.

(T. D. 29512—G. A. 6859) *Magnesia rings.*

1. MAGNESIA RINGS—BISQUE.

So-called magnesia rings, used as part of gas-light burners, held upon the evidence to be bisque, and hence dutiable under the specific provisions of paragraph 96, tariff act of 1897.

2. CASES REVIEWED.

Previous decisions of the Board and the courts reviewed, and Crawford *v.* United States (T. D. 28539) distinguished upon the facts.

(T. D. 29516). January 29, 1909.—No. 20562.—RESIN PITCH.—Protests 291529, etc., of R. F. Lang (New York).

So-called resin pitch classified as a chemical compound under paragraph 3, tariff act of 1897, was claimed to be dutiable as an unenumerated manufactured article under section 6. Protests sustained.

CHAMBERLAIN, *General Appraiser*: * * * Samples of the merchandise were submitted, at the request of the importer, to the United States chemist at the port of New York for analysis; and based upon his evidence, we find the merchandise to be a mixture of oxidized resin and vegetable oils, the product having no well-recognized composition of chemical formula. It is our opinion, therefore, that the merchandise is not a chemical compound, for it has been repeatedly held that a mixture where no chemical union results is not a chemical compound within the meaning of paragraph 3. G. A. 5832 (T. D. 25733); G. A. 6269 (T. D. 27051); G. A. 5718 (T. D. 25410).

(T. D. 29518) *Glycerophoshate of lime.*—KLIPSTEIN *v.* UNITED STATES.—U. S. Circuit Court Appeals, Second Circuit. January 12, 1909. No. 127 (suit 5205).

GLYCEROPHOSPHATE OF LIME—CHEMICAL COMPOUND—MEDICINAL PREPARATION.

Glycerophosphate of lime, which, though occasionally dispensed medicinally in its imported form, is almost always used in combination with other drugs in the preparation of elixirs, is not a medicinal preparation within the meaning of paragraph 67, tariff act of 1897, but is dutiable as a chemical compound under paragraph 3.

APPEAL from the circuit court of the United States for the southern district of New York.

[Decision adverse to the Government.]

The decision below (T. D. 29100) affirmed a decision by the Board of United States General Appraisers, which had affirmed the assessment of duty by the collector of customs at the port of New York on merchandise imported by A. Kilpstein & Co. Abstract 17921 (T. D. 28687).

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EDITORIALS.

READJUSTMENT.

WE are living in the days of the flying machine. Darius Green has been vindicated, and again we attempt to adjust our articles of faith so as to be more liberal. In chemistry the mental equilibrium which represents the balance between what we consider the possible and the impossible is disturbed by the apparent genesis of some of our sacred elements. This disturbance is counterbalanced by failures to confirm, but the thing is in the air. The machine has apparently operated, the faith has been adjusted, and this particular chemical guiding-star of specific individuality of the elements has become a comet receding along one of those hyperbolic paths which will continue to carry it away from us.

How much more readjustment must the chemist make? He has always been in the act of discovering or of being surprised. Yet he cannot discount the future to any extent. He knows that a microscopic cell contains in the chromosomes of its almost invisible nucleus something in material, or arrangement, which determines heredity. Development may make of it a polyp, an onion, or a man. The product will be further possessed of numberless characteristics which must have been dominant in the egg, and were determined by at least many of the ancestors of the new individual. Where was it? How fine is material? The theory of finite limits in fineness may be wearing out. A theory is a suit of clothes covering a nakedness. It is criminal to appear to be without it. It is foolish to change it too frequently, and it is slovenly to neglect it. We have used the atomic theory because it covered for a time the nakedness we recognized, but it must apparently be changed. Generally it is easier to patch than to renew, and he is a bold chemist who, knowing the style, dares renew entirely his theory. The atoms in some form will continue to be at least a covering below which other changes may be made, without an essential alteration of the previous outer design of the suit.

Are we not justified in believing that no limits of fineness are to be placed; that in fact all possible conceptions of finality are in us and not in Nature? If this were so, the continual change in our theories might be explained. As we develop we widen our horizon, and this is limitless. Is there any greater reason for assuming that the electron of conducting gases is the limit of their divisibility than that this was set by the chemist's atom of the recent past? The energy conceptions of matter which tend now to make us brush up our definition of matter, are as surely a transient state as were the elements earth, fire and water. What we always seem to gain by these pioneer efforts is a sort of trail-blazing which shows us a way to further co-ordination of facts, to simplifying mental processes and to prophesying. It has its great good for a certainty, not as an end, but as a means.

W. R. WHITNEY.

CHEMICAL SOCIETIES IN AMERICA.

THE opinions of *Electrochemical and Metallurgical Industry* on National Chemical Societies were published in a recent editorial, in part as follows:

"The Baltimore meeting was exceedingly well attended. There was much rejoicing in the new spirit of activity manifested in the American Chemical Society. * * * .

"Any special brand of chemists may now find a certain limited degree of recognition and furtherance within the American Chemical Society under its new benevolent paternal policy. It is not fair to deride this new policy as a lucky afterthought and the new spirit of progressive activity as forced upon the Society by outside developments. * * * .

"In addition to the American Chemical Society and the American Institute of Chemical Engineers, there is the American Electrochemical Society, now seven years old and rapidly growing in membership and prestige. In all we have, therefore, now, three national chemical societies in this country. But the field is so broad that there is open for each of them a career of usefulness and activity, with glory enough for all. Though independent, they all could and should co-operate in a fine liberal spirit to promote the common interests of chemistry, each in its own sphere of influence. It is high time that narrow jealousy should cease. It should no longer be possible or practicable for a distinguished industrial chemist to rise in an important committee meeting with the complaint that electrochemical engineers and inventors get all the public recognition and the poor 'pure chemists' get nothing. Those over-zealous members of the American Chemical Society who even now, again and again, bring forward the suggestion of absorbing the Electrochemical Society, should finally learn that such a scheme is, to put it mildly, an anachronism. And the formation of the American Institute of Chemical Engineers should also be taken as an accomplished fact. The American Chemical Society can find no better friends than among the founders of the Institute. It is all very well to speak of the tendency of the times to form commercial combinations and trusts for manufacturing on a large scale. But science, pure and applied, is promoted not in such a way. What counts here is individuality, the man as man. Great advances are made by opposing individualities. For the promotion of science and engineering, even in a limited field like chemistry only, nothing could be worse than the combination of the various scientific and engineering societies into one unit, with one publication committee and an editor in charge who as a practical dictator would determine what is suitable for publication and what not. It is unnecessary to add another word."

After making allowance for the ambiguities of generalization, there remain among these statements several which may be fairly questioned. Not a few of the conservative members of the profession dissent from them. The Western Society of Technical Chemists and Metallurgists, national in everything but name and with a membership approximating that of the American Electrochemical Society and also the American Leather Chemists' Association with a larger membership than the American Institute of Chemical Engineers, may well be included in the list of American Chemical societies. Each of these publishes a monthly journal.

"Science pure and applied" is not promoted by combination or at least by large combinations. "What counts here is individuality, the man as man." We honor the individual who accomplishes great works unaided by organization or communion with his fellow workers, the Palissy whom nothing can defeat; but it is unwise to belittle the value and importance of scientific organization on the large scale. If we are progressing scientifically to-day, we are progressing because of far-reaching scientific combination. Although the factors of progress are various, our progress will advance or decline with the integrity and continuity of our organization.

The editor of *Electrochemical and Metallurgical Industry* seems to forget that combination for purposes of publication is especially necessary, and that whether this combination is secured by means of the subscription list of a journal privately conducted or by means of a society more or less national or international in its character and organization, is a matter of detail. The purpose of scientific publication must be to secure as wide a dissemination as possible of the results of scientific work. Two years ago some of the officers of the American Chemical Society attempted to secure a co-operation between that society and the American Electrochemical Society with a view to securing the circulation of papers published by either society throughout the membership of the other. The difficulties of securing such a co-operation appear to be insurmountable, but the members of the American Chemical Society certainly have no wish but for the best success of the Electrochemical Society. The success of that society is evidence that it has filled a useful place in the development of our scientific activities and there is no doubt that it will continue to do so. At the same time it seems unfortunate that many scientific papers published in America reach only a small fraction of the chemists to whom they would be most useful. It is because the American Chemical Society has, for the first time in the history of American science, succeeded in publishing chemical journals which have secured a very large circulation that the society has an especial right to ask for the support of all American chemists.

The picture of the combination of the various scientific and engineering societies of this country into one unit with an editor as "practical dictator" is a flight of fancy too great for us to take. Certainly the editors of the American Chemical Society are by no means "practical dictators." They are, in the first place, elected annually by a council of the society consisting of sixty or more representative chemists. Any attempt on the part of the editors to follow a course which was distasteful to a majority of the chemists of the country would be quickly followed by the appointment of other persons in their places. In addition to this, each editor has associated with him a number of associate editors, to some of whom every paper is submitted before publication and in case of any difference of opinion between the editor and associate editor to whom the paper is submitted, the question may be referred to the president of the society for decision. In some cases a doubtful paper has been submitted to nearly or quite the whole board of associate editors, and a practically unanimous opinion was secured before the paper was rejected. A democratic organization of the character of the American Chemical Society would seem to secure the rights of authors at least as well as they can be secured under the plan of a journal conducted as a private enterprise.

All the funds of the American Chemical Society go to the furtherance of chemistry in America. If the funds are increased as by an increase in membership or by advertising, all chemists will be the gainers. The work of its editors is largely a labor of love.

In the days when chemistry was little honored in this country, when chemists were few, salaries low, and support meagre, a few unselfish self-sacrificing men gave their time and money to the cause of the organization now known as the American Chemical Society, that all chemical research might be advanced and that the standing of all chemists in the community might be raised. In the days when there was no profit in publishing chemical journals, they published the *Journal of Analytical Chemistry* and later the *Journal of the American Chemical Society*. Their offense, if offense they committed, lay in publishing too much rather than too little; in printing the work of uncertain value rather than in excluding it.

The American Chemical Society favors and will always favor any movement among chemists which will advance the interests of chemistry and chemists in the best possible way. In the matter of publication, it believes the best interests of chemists are conserved by a large organization. This is not an hypothesis but a matter of simple calculation. The society supports all movements looking to the benefit of chemistry. Its friends are the friends of chemistry in America.

W. D. Richardson.

ORIGINAL PAPERS.

THE RARE EARTHS—THEIR PRODUCTION AND APPLICATION.[1]

By H. S. Miner and M. C. Whitaker.

Received January 16, 1909.

The term "Rare Earths" was given originally to a group of earths of which but little was known and which we were accustomed to think was very sparsely appropriated throughout the mineral kingdom. At the present time, however, it is conceded that while not the most abundant of the elements which Nature has provided, yet they are of wide distribution; and when we consider that many of these elements are now dealt in by tons and the minerals containing them are dealt in by hundreds of tons, the term "Rare Earths" appears to be a misnomer. Instead, therefore, of conveying the original idea of scarcity, this term now conveys the idea of a fairly definite chemical classification, just as does the term the "Alkaline Earths" or the "Iron Group."

The late Prof. Mendeléeff has described this group of elements as one "which in their sesquioxides, present basic characteristics of a more energetic nature than those shown by alumina." The elements of this group as recognized by the International Committee on Atomic Weights, both by their chemical reactions, and by natural occurrence, fall into the following general classifications:

Cerite Group.—Cerium, Lanthanum, Neodymium, Praseodymium, Samarium, Gadolinium.

Ytterite Group.—Yttrium, Erbium, Terbium, Ytterbium, Scandium, Thulium, Dysprosium.

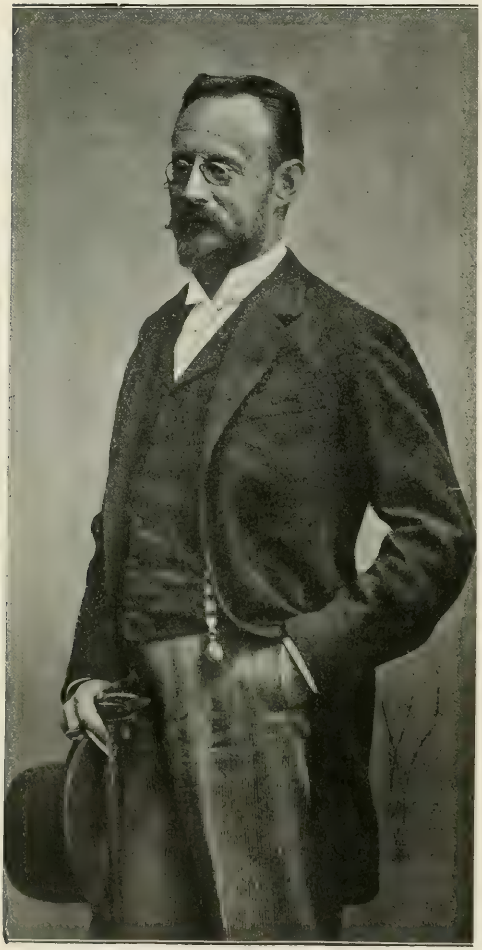
Thorium.

Zirconium.

The beginning of the study of this group of elements is traceable back about one hundred and twenty years and probably begins with the discovery of zirconium by Klaproth in 1788. He also

[1] A paper read before the New York Section of the American Chemical Society, Friday evening, December 11, 1908.

discovered cerium in 1803, while Berzelius just ninety years ago made the still more important discovery of the element thorium. From these beginnings the work was followed up all through the last century, and who shall say that the end of the chapter has been reached?



Dr. Carl Freiherr Auer von Welsbach.

Claims have been recently made that some of these supposed elements are not elementary in their character after all, but are mixtures of two or more elements. This claim is certainly supported by precedent, notably the work of Dr. Auer when, after forty-three years, from the didymium of Mosander he produced neodymium and praseodymium. In view of these results and other work of a similar nature, it is not too much to believe that others of these supposed elements, and not improbably even the two just mentioned, are complex in their nature.

I have alluded to the fact that the elements once noted for their rarity are very widely disseminated throughout the mineral world. It has been claimed that the fifteen elements which I would include in the classification of the "Rare Elements" are found in over one hundred different minerals. These minerals have been found scattered over the whole globe. Lines of several of these elements have also been found in the solar spectrum.

The wonderful discovery made by Dr. Auer transformed the group of elements which had been long known as the "Rare Earths" from scientific curiosities into materials having a very practical value. Minerals containing certain of these elements had been known to scientists for more than one hundred and fifty years; but beyond a very limited use in the preparation of a few medicinal compounds no practical value had been developed for any of them.

The first Welsbach mantles required principally lanthanum, cerium and zirconium, elements which existed in large quantities in the Swedish mineral cerite and in zircon. An ample supply of both of these minerals was found and large quantities of cerite were mined in Sweden, and soon sufficient zircon was produced in Norway and in North Carolina to meet the demands of the incandescent gas lighting industry. This type of Welsbach mantle also developed a demand for the mineral allanite and a large deposit of this rare earth mineral was discovered in Virginia.

The invention of the thoria-ceria mantle, composed of practically 99 per cent. of thoria, produced an immediate and urgent demand for minerals rich in that element. At that time the Norwegian mineral thorite, containing about 50 per cent. of thoria, seemed to be the most hopeful source of supply. Diligent search, however, failed to discover a sufficient quantity to supply more than a small fraction of the thoria needed. Many other minerals, of course, were known which contained thoria, most of them in much smaller percentages than thorite, but none of these, with the exception of monazite, had been found to exist in commercial

quantities. Deposits of monazite sand had been discovered in North Carolina and in Brazil, and considerable quantities had been mined for use in the manufacture of the lanthanum-cerium-zirconium mantle. Lanthanum and cerium were the ingredients which had at first made the monazite of value and the thoria content had been practically overlooked and discarded. Finding that minerals rich in thoria were not commercially available more careful attention was directed towards the deposits of monazite already developed, with the result that large deposits were found in both of these localities. Though by no means an ideal mineral, yet being the only one found in paying quantities, it soon became recognized as the commercial source of thoria.

Monazite had been known since early in the nineteenth century and the fact that its name signifies "to be solitary" indicates that at the time of its discovery, at least, it was considered to be one of the very rare minerals. Since its first discovery monazite has been identified in the rocks over a large part of the earth's surface. Usually, however, it is found to compose but a minute portion of the rock and in many instances its presence can only be detected by the use of the microscope. The monazite deposits of commercial importance are those occurring in the placer sands of the streams and the adjoining bottom lands, and in certain beach sands along the seashore. Geologists tell us that such deposits can only be formed in countries which have not been subjected to the tremendous eroding influences of prehistoric glaciers during the ice age.

Monazite, in its original formation, occurs in rocks of the granite class and in many places these rocks have been decomposed by the action of weathe ing, and the grains or crystals of monazite thus liberated are collected in the stream-beds or bottom-lands below. As the monazite moves to its bed, by the action of running water, it undergoes a process of sorting and concentration, the lighter minerals being washed away, leaving the heavy monazite in a pocket with other heavy minerals, forming a "placer" deposit.

Knitting mantle fabric.

Monazite crystallizes in monoclinic crystals and has a hardness of from 5 to 5.5 and a specific gravity from 4.8 to 5.3. It is generally found in small grains or crystals; in fact, the grains are so fine that the mineral is commercially known as "monazite sand." Large masses and crystals have been found in Norway, though in this form the mineral is a very great rarity. Monazite is found in a variety of colors, such as light yellow, red, brown, green, buff and a great variety of intermediate shades. Chemically speaking, monazite is essentially a phosphate of the rare earths of the cerium group, and though its various components may vary considerably in different samples, a fairly typical analysis would be as follows:

Phosphoric anhydride	28	per cent.
Cerium oxide	30	"
Lanthanum oxide	14	"
Neodymium oxide / Praseodymium oxide	16	"
Thorium oxide	5	"
Yttrium oxide	2	"
Iron oxide / Calcium oxide	5	"
Etc.		
	100	"

The discovery of the application of monazite to the incandescent gas lighting industry was a great incentive to the search for this mineral, but even after nearly twenty-five years, the only deposits of commercial importance are those originally known in the Carolinas and in Brazil. It is true that the borders of the deposits as originally known in both these localities have been very much extended, and far richer beds have been uncovered

than were originally known to exist; yet until this date all the monazite sand used in the manufacture of incandescent gas mantles comes from either the Carolinas or from Brazil.

The monazite district in the Carolinas comprises approximately 3500 square miles of the border region of both North and South Carolina, and lies chiefly in Burke, McDowell, Rutherford, Cleveland and Polk Counties of North Carolina, and in Spartanburg and Greenville Counties of South Carolina, though many of the counties bordering on these mentioned contain deposits of this mineral. The monazite is found in the sand carried down by the rivers and "branches" of this district, and in the gravels underlying the "bottom" land bordering on these streams. Many of these streams and "branches" had been originally worked for gold, and the "tailings" of these placer operations were early found to contain monazite in paying quantities. The natural concentrates of the stream-beds were about the first deposits to be worked commercially in this region, the plan of operation being similar to that of gold placer-mining with the well-known "Long Tom" or rocker apparatus. By this process, the water from the "branches" is temporarily deflected from its channel, and is used to wash and concentrate these deposits in sluice-boxes before it returns to the original channel farther on. The sand and gravel are shoveled on to a perforated plate, and washed in the streams of water, allowing the lighter and finer impurities to float away, and permitting the heavier particles, principally monazite, to settle and remain in the bottom of the boxes.

Saturating mantle fabric with lighting fluid.

Stream beds are now so far exhausted that attention has to be paid to the adjoining "bottoms." The monazite is found in the gravel and there is usually a heavy "overburden" to be removed before this gravel can be reached. Here again the operation of placer gold mining is followed, except that in many cases the work has to be conducted methodically, since much of this bottom land has a value for tillage purposes. The purification of the washed sand is continued by various concentration devices, such as Wilfley tables or magnetic separators, by which most of the other impurities are removed, and the final product contains from 90 to 95 per cent. pure monazite, in which form it is ready for the market.

The largest known deposits of monazite sand are those which are found in Brazil, and these deposits supply practically all the monazite that is used in the European thorium factories. The principal Brazilian deposits are found on the coast of the provinces of Minas Geraes, Sao Paulo, Rio de Janeiro, Bahia and Espirito Santo. The monazite here is really a beach sand, being found either on the shore of the ocean, or in the lowlands immediately bordering the shore. The method of mining the Brazilian sand is very similar to that in vogue in North Carolina.

The annual production of monazite sand has very rapidly increased since the introduction of the Welsbach light. From the very small quantity of sand which was mined in the year 1888, the output has increased, until at present the annual transactions in this mineral are rated by the thousands of tons. Thus the day has passed when monazite sand can be spoken of as a "rare" mineral.

A new mineral was discovered a few years ago in the island of Ceylon, which has a composition rendering it an almost ideal source of supply for incandescent mantle chemicals, could it be procured in sufficient quantities. This mineral is thorianite and it is composed essentially of uranium and thorium, the latter comprising from 60 to 75

per cent. of its composition. As in this mineral the element sought is its essential constituent, it is to be regretted that as yet it has been found only in this one locality, and there only in small quantities.

As the chief use of the rare earths is found in the manufacture of incandescent gas lights, it might not be inappropriate for us to consider, at least, some of the salient points in the development of this system of illumination which has such a broad application.

Without any attempt to give a complete history of gas illumination,[1] or even to fully describe the very interesting development of incandescent gas lighting, I would say, that the discovery by Goldsworthy Gurney in 1826, that a lime cylinder could be raised to incandescence by the flame of an oxyhydrogen blowpipe first called attention to the fact, that certain refractory substances, when heated to a high temperature, possessed light-giving qualities. Thomas Drummond was supposed to be the first to make practical application of this discovery, which he did in the survey of Ireland, by the lamp which bears his name, which was used in connection with the heliostat for locating distant stations, and which has been in continuous use ever since as the "lime" or "calcium" light. Developments along this particular line have been confined to varying the size, shape and composition of the incandescent body, the lime being replaced by magnesia and later by zirconia.

In about 1830 we find that the municipality of Paris was attempting to light their streets by using little buttons of zirconia, heated to incandescence by the combustion of gas and oxygen conveyed to the burners in separate pipes. The excessive cost made the early abandonment of this system a foregone conclusion.

In 1839 Cruickshank took out a patent in England for a cage or mantle of fine woven platinum wire, which was of the proper shape and size to thoroughly envelop the outer portion of the flame, and be just enough smaller than the flame to be thoroughly immersed in it. Cruickshank soon realized that platinum was not the ideal material for light-giving purposes, for he says "although the light emitted by platina at a high temperature is very bright, it is inferior to that of lime and other earths at the same temperature." He tried to combine the strength of his platinum with the light-emitting properties of these earths, but found it was impossible to make his paste adhere to the surface of the platinum for any length of time.

The introduction of non-carburetted water-gas by Gillard in 1848, furnished a new incentive for invention, for though this gas which Gillard used in connection with his iron foundries at Narbonne, would be adapted for heating purposes it would have no application as a source of illumination. The inventor of this process of gas manufacture would naturally be expected to have the greatest interest in this development, and we are not surprised to find Gillard himself, devising a cap or mantle of fine platinum wire which he suspended in the flame of his "blue gas," and it is said that for some months this method of lighting was used at Passay and at Narbonne, but the rapid deterioration of the platinum mantle made this experiment very short-lived. The mantles not only lost their light-giving power, but finally became so brittle that they fell to pieces, and we are not surprised that Gillard's experiment should eventually fail as did that of his forerunner, Cruickshank, nine years before.

Sewing and tying mantles.

[1] See information given by Dr. Doremus in the discussion that follows.

Until the early 50's, the only non-luminous flames that could be produced were these of the spirit lamp and of uncarburetted water-gas, but at about this time Prof. Robert W. Bunsen, while planning and fitting out his great laboratories at Heidelberg, incidentally developed the burner that now bears his name, an invention which has done more for the gas industry than almost any other discovery or invention connected with it. While considering the methods of heating that should be adopted on the working benches of his new laboratory, it is said, that one of Bunsen's assistants pointed out to his chief that a non-luminous flame could be produced by passing coal-gas a short distance through the air, and then taking it through a piece of wire gauze. Seeing at once the importance of this suggestion, Bunsen brought his marvelous manipulative skill to bear on the problem, and in a few weeks produced the "Bunsen" burner. It is of interest to know that the assistant who made this suggestion, was later known as Sir Henry Roscoe.

Modeling and hardening mantles.

It is not the purpose of this article to describe in detail the work done by the multitude of investigators, who from time to time entered this new field of research, but only to mention some of the characteristic steps leading up to the incandescent gas light of to-day.

Notwithstanding the discouraging results obtained with platinum as an illuminant even as far back as 1839, we find that it was persistently tried for fully fifty years by a long line of inventors. Gillard, whom we noted as using a platinum mantle on the "blue" water-gas which he invented in 1848, continued to use it as late as 1865 in Paris and in Narbonne. He was followed by Lewis, Sellon, Moreau and others, but their lamps all met the same fate as did the first invention of Cruickshank.

Clamond, who had been working on this problem for a number of years, brought out a lamp in the early 80's in which the illuminant consisted of an earthy basket. His first lamp was of the inverted type, and the basket was held in position by a platinum skeleton, but he soon changed this lamp to the erect type, and made his earthy basket of a conical shape. The Clamond basket was made from a pasty mixture of magnesia, the fibers being wrought into the desired form while in the flexible condition before ignition. Various modifications in the composition of the basket were made, in some of which zirconia was used, but the system was destined to be soon supplanted.

Other experimenters attempted to manufacture a mantle, by spreading an earthy paste in a thin layer over a form, and then perforating the dried sheet, which, after ignition, was suspended in any non-luminous flame, but this system was soon found to be impracticable.

The next form of an incandescent lamp to receive a practical test, especially in the fuel-gas plants of this country, was that designed by Fahnejelm, which may be described as a bundle of needles of refractory earthy material, arranged in the form of a comb, and suspended in the non-luminous flame of the bats-wing type. Fahnejelm preferred magnesia for his base material, though he mentions a number of other possible oxides. He forms these oxides into a paste and at the same time incorporates a small quantity of flux to make them stronger and more pliable when heated in the flame. These lamps were given a thorough test in connection with the fuel-gas plants in the Hyde Park Plants at Chicago, at Jackson, Mich., and at other places, but were soon discarded.

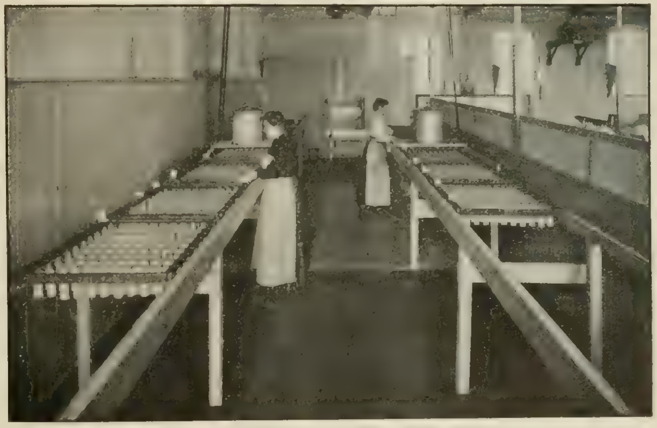
Stewart devised a type of burner, which embodies the Fahnejelm idea of pencils or needles of refractory

earth. He reduced the mass in his pencils, however, by making them tubular in form so as to increase the lighting efficiency, and caused the gas to issue from a series of small orifices, so as to form a number of independent blue flames in close proximity to the incandescent tubes.

More than half a century has elapsed since the first incandescent gas light was invented, and during that time many interesting developments have been made, the most important of which we have attempted to enumerate. Important as these inventions were, however, none of them constituted a satisfactory incandescent gas light for the crux of the situation had so far eluded all investigators. It remained, therefore, for the young Austrian chemist, Dr. Karl Auer, to conceive the idea of impregnating a fabric with salts of the rare earths, burning out the organic material and so forming a skeleton or mantle of the rare earth oxides. About the year 1880, Dr. Auer was engaged in investigating the chemistry of the rare earths in Prof. Bunsen's laboratory in Heidelberg. In order to get the material in a more attenuated form, he says: "It just occurred to me, by chance, to impregnate a cotton webbing with a solution of these salts, and then to burn out the cotton. It was most probable that the experiment would fail, as the remaining earths were not liable to stick together after the cotton was burned out, but after all, the experiment was a success, and the earths retained the form of the webbing."

In his further experiments he found that lanthanum oxide not only formed a coherent body, but gave a very intense white light, and it was this fact that inspired him with the idea of using the rare earths for lighting purposes on a large scale. A mantle made from this material, however, soon decomposed and crumbled to a powder. Realizing the necessity of combining the lanthanum oxide, with its demonstrated light-emitting qualities, with some other substances that might not so easily absorb water vapor or carbonic acid, he first experimented with magnesia, but finally adopted zirconia as the substance best adapted for this work; and, based upon this composition, the commercial manufacture of incandescent mantles was begun. The mantles gave from 30–32 C. P., with a consumption of three cubic feet of gas per hour. Finding it necessary to improve this efficiency, Dr. Auer experimented with all possible material in nearly every conceivable combination, but with no essential improvement. Finally, in duplicating some of his earliest experiments, he noted that thorium oxide possessed desirable qualities.

In resuming these experiments with thorium it was necessary to prepare more material, and in doing so a very remarkable phenomenon appeared, the purer the thorium preparation, the less light emitted. Feeling convinced that his thorium had been increasing in purity as his candle-power had been diminishing, he began to experiment with the portions that had been removed, by successive purification processes. Here he found evidence of a special light-giving body, which was demonstrated to be cerium. With this information, and a few synthetic experiments by the addition of pure cerium to pure thorium, the brilliant light which we have to-day, was obtained. The incandescence of the new mantles exceeded that of the old threefold. The lasting qualities were also very much improved, and finally a satisfactory incandescent gas light was obtained.



Coating mantles.

The advent of the thorium-cerium mantle served to give the incandescent gas-lighting industry the greatest impetus that it had ever received throughout its history. The efficiency of the old lanthanum-

zirconium-cerium mantle was increased by this invention to fully 22 candles per cubic foot of gas consumed. A pure thoria mantle, as has been stated, gave but very little light, but strange to say only about 1 per cent. of ceria was sufficient to produce this marvelous efficiency. The addition of more than this amount resulted in a lowering of the candle power, but within certain limits this loss in light was fully compensated for by an increase in the yellow color of the light.

Trimming and inspecting mantles.

While every conceivable substance has been experimented with, as an excitant upon a mantle with a thorium base, and many materials have been found that possess this quality to some degree, yet no substance equals that which was found to be the excitant in the original substance upon which Dr. Auer worked, cerium. The highest candle-power, on an average, is obtained with the addition of about 1 per cent. to 1.25 per cent. of ceria, though this amount is dependent upon the character of the fiber of the mantle itself. Manufacturers are often compelled, however, against their best judgment, very frequently, to supply mantles of very much lower percentage of ceria than those indicated as giving the maximum initial efficiency. The increase in the proportion of ceria increases the yellow rays in the spectrum of the mantle, producing a better quality of light, and making a mantle of superior quality and more permanent and uniform light-giving power.

Many attempts have been made to improve upon the thoria-ceria mixture of Welsbach, and I presume that the end of these attempts is not yet. But thus far, pure thoria and pure ceria are the mainstay of the incandescent mantle business.

There is no more important constituent entering into the manufacture of mantles than the thread which forms the base from which the mantle is started. Various fibers are used in the spinning of these threads, but the only ones of any commercial importance are cotton and ramie. Artificial silk might be mentioned as of experimental importance. Furthermore, there are a number of kinds of thread made from the various different materials. For example, a thread may be a single twisted cord, or it may be two cords twisted together, in which case it is known as a two-cord thread; or it may be three cords twisted together in which case it is known as a three-cord thread; or you may have four-cord threads or six-cord threads. Threads of more than six cords are not made in the sizes used for mantle-making. The cost of the thread varies with the quality of the material from which it is made, and also with the number of strands twisted together to form it.

While extensive studies have been made of other fibers than those mentioned here, results have not been obtained which would justify their use in the manufacture of mantles. Of the three materials—cotton, ramie and artificial silk—cotton is used almost exclusively in the United States; both ramie and cotton are used abroad; artificial silk is only in the experimental stage. In view, therefore, of the importance of cotton as a base for the manufacture of the American mantles, we will confine the discussion to threads made from this substance.

Inasmuch as the texture of a finished mantle reflects every detail of the basic fabric from which it is made, the kind of a thread, the quality of the material used to make it up, and the uniformity of its size, have a direct bearing on the physical and candle-power life of the mantle. It is necessary to use a thread of uniform diameter with a maximum number of cords and made from a material with a

long staple in order to produce a mantle of the highest quality. In the manufacture of mantles of different qualities to be sold at different prices, the distinction starts in with the quality and kind of thread used. In the cheap mantles the three-cord and four-cord and in some cases six-cord threads are used which are made from the lower grades of cotton. The highest grades of mantles require the use of a carefully made six-cord thread of uniform size made from the best quality cotton.

One of the most important operations in connection with the manufacture of mantles from cotton or any of the other basic fabrics is the washing process. It can be taken as an axiom in mantle-making that anything which tends to introduce the slightest chemical impurity into the finished mantle will work great injury to the product. Starting with the thread, therefore, we remove every possible trace of mineral impurity. The purest cellulose fiber which you have ever seen is absorbent cotton, such as that on the market for medicinal and surgical uses. On analysis, this absorbent cotton shows a mineral impurity of from 0.05 to 0.06 per cent. Ordinary cotton threads, such as are used in sewing, will show a mineral impurity of practically 0.5 per cent.

The washing process used to produce these results must necessarily be very efficient, as there is a marked difference between washing loose cotton, like absorbent cotton, and the tightly twisted threads in the knitted fabric used in the manufacture of mantles. The method of washing is a carefully designed combination of a chemical and mechanical process. The work is done in a room or building especially constructed with a view to carrying out an operation requiring exceptional cleanliness. The chemicals used are the purest substances obtainable; the solutions are all made in distilled water, and all of the mechanical appliances are constructed from materials especially chosen to resist the action of the various chemical agents employed. This equipment must be of such a character as to produce not only the highest attainable degree of purity in the fabric, but must produce it with absolute uniformity. It is obvious that perfect washing of some lots of fabric, with the imperfect washing of others, would materially affect the uniformity of the product.

Saturating is a comparatively simple process, where the thoroughly dried webbing is placed in a suitable vessel and covered with the lighting fluid. The fabric is allowed to remain in the lighting fluid until it is thoroughly saturated. The excess of fluid is then drawn off and the fabric is put through an equalizing machine piece by piece. The amount of substance to be used in the mantle is regulated at this point. In the inferior grades of mantles the quantity used is cut down to a minimum and is controlled only by the limit to which the manufacturer can go and produce a mantle which will hold together during the succeeding manufacturing operations. In the highest grades of mantles, the amount of lighting fluid used is based upon a careful consideration of the amount of material required to produce a mantle of the highest physical and candle-power life.

Packing mantles.

The next step in making a mantle is the formation of the head and loop. This operation is accomplished by folding-in one end of the tubular fabric and uniformly plaiting the folded portion and sewing an asbestos cord through the plaits. The asbestos cord used for this purpose must be made from a carefully selected long staple asbestos fiber, and must contain a minimum amount of cotton binder. In the manufacture, as well as in

the use of the mantle, the asbestos cord is subjected to an intense heat, and unless it has been made from a long staple asbestos fiber with a minimum amount of cotton binder, it will disintegrate and render the mantle useless. The American manufacturers of this asbestos cord obtain their supply of raw material from Canada.

The method of branding mantles is very simple. The principle on which it is based is governed by the fact that the oxide of thorium and cerium is white, and in order to form an indelible brand on the mantle it is only necessary to place over this white oxide some chemical which has a colored oxide, as, for example, iron, which gives a reddish brown oxide, or didymium, which gives a dark brown oxide. Didymium gives the most permanent brand and is the substance most generally used. The brand is put on the saturated fabric by using a rubber stamp in conjunction with a stamping pad which has been saturated with the branding fluid.

The mantle is now suspended in a suitable hood and a torch applied for the purpose of burning out the cotton. The ignition is usually made at the top near the asbestos cord, so that the burning out will be gradual and not subject the remaining ash fabric to any undue strain. After the cotton is completely consumed the ash of thorium and cerium oxides hangs in a soft, shapeless, flabby condition, and presents a very remote resemblance to a mantle. It is a remarkable phenomenon that this ash should have sufficient cohesive power to hold together after every vestige of the original cotton fabric has been burned away.

When Dr. Auer first explained his idea for making a mantle to Prof. Bunsen, that famous teacher replied: "It is extremely doubtful if the ash can be made to hold together." This opinion was based upon Prof. Bunsen's knowledge of the general characteristics of metallic oxides, but the combination of metals with which Dr. Auer was working were exceptions to the rule. The Incandescent Gas Lighting Industry rests upon this remarkable exception.

The operation also has some remarkable features. After the cotton is completely burned out in the process just described, the soft, flabby ash is carefully adjusted over a blowpipe. The operator of this device controls levers which raise and lower the mantle and which adjust the gas supply and the air supply to the blowpipes. In some cases the gas issues under a pressure of several pounds to produce the intense flame required, but in either event the adjustment of the flame and the control of the position of the mantle is entirely in the hands of the operator. Under the influence of this intense blast flame, the flabby ash left when the cotton fabric was burned out is blown (by the proper control of the flame) into the shape of a finished mantle and is changed from its soft pliable state into a hard resilient form. This operation requires greater skill and experience than any other work connected with the manufacture of mantles.

The mantle is now "coated" to preserve the ash in the exact state in which it left the hardening operation while it is going through the inspecting, trimming, packing, transportation and installation stages. This coating or collodion, as it is usually called, is made from soluble cotton.

In the next step the mantles are taken out of the drying chambers and placed before inspectors, whose duty it is to trim them to uniform length and carefully inspect each individual mantle. This is an operation which is regarded as very important. It is an easy matter for people handling collodionized mantles to injure them, and yet the injury will not show until the coating is burned off. Furthermore, the inspection is not entrusted to irresponsible employees, and the greatest amount of care and supervision is devoted to this branch of the manufacture of mantles.

The mantles go to the Packing Department, where they are packed according to the desire of the consumer. The market is supplied with Loop mantles, Double Wire-Cap mantles, Centre-Support Cap mantles and Ring-Top mantles.

In summing up this superficial outline of the process for making mantles, it must be apparent that it is a process of great complication. These complications are divided into two distinct classes:

First.—The chemical problems which have to be solved and controlled.

Second.—The problem of supervising and controlling the work of the employees in the various different operations.

The first of these problems is under the control of a chief chemist and staff, who supervise the manufacture and use of each one of the chemical constituents entering into the make-up of these goods. Every operation involving a problem in chemistry or physics is carefully studied out and conducted under their supervision and direction.

There is no chemical manufacturing industry which requires such a large staff of trained experts

as the manufacture of mantles and the raw materials for their production.

The second division of this subject is of no less importance than the first. There are many critical operations in the manufacture of a first-grade mantle. By a critical operation, I mean an operation which if not properly conducted will result in the production of an inferior piece of goods.

It is necessary, therefore, to have not only a carefully organized supervising staff of exceptionally efficient foremen, but also to have a high grade of intelligence in the working force and to teach them to appreciate the importance of the work entrusted to them.

The amount of skill required from the employees and the grade of intelligence demanded will exclude mantle-making from that class of manufacturing industries which use cheap and ignorant help. The proportion of pay-roll which goes to the supervising staff is greater in mantle-making than in any other manufacturing line. The greatest factors contributing to the success of the American mantle manufacturer are:

First.—A thorough study and understanding of the technical difficulties involved in the various different processes.

Second.—A carefully organized and intelligent suvervision of every process.

Third.—The high intelligence, integrity and skill of his employees.

Furthermore, I laid down in the beginning the axiom that any impurity introduced into the mantle in any of the processes would seriously affect the finished product. This makes it apparent that absolute cleanliness of the entire plant, of every operation and of every operator is imperative. In addition to this, the raw materials in the process must be made under the direct technical supervision and control of the mantle manufacturer.

Discussion by Dr. Charles A. Doremus: Dr. Miner has referred to Drummond as the first one to obtain an incandescent light. He will pardon my reading from a memoir by Prof. Robert Hare. It is entitled "On the Supply and Application of the Blowpipe," published by order of the Philadelphia Chemical Society, 1802.

Hare made a report to the Society on December 10, 1801, and exhibited experiments with his new apparatus which consisted not only of a blowpipe but also of a hydrostatic reservoir for holding the hydrogen and oxygen in separate compartments to be delivered as required.

On page 29 of this pamphlet the following description of some of his experiments occurs:

"The cock of the pipe communicating with the hydrogen gas was then turned until as much was emitted from the orifice of the cylinder as when lighted formed a flame smaller in size than that of a candle. Under this flame was placed the body to be acted on, supported either by charcoal, or by some more solid, and incombustible substance. The cock retaining the oxygen gas was then turned until the light and heat appeared to have attained the greatest intensity. When this took place, the eyes could scarcely sustain the one, nor could the most refractory substances resist the other." Hare has in many places in his subsequent writings made full claim to the "lime light."

Discussion by Dr. Morris Loeb: In addition to the hypotheses mentioned by the first speaker, it has, at times, been suggested that the oxide of thorium forms a complex with the other oxides, and that luminosity accompanies isomeric changes in this larger molecule. It has occurred to me that the conversion of heat into luminescence might be well explained on a hypothesis similar to that which was, I believe, first advanced by Huggins, for the explanation of fluorescence by the existence of very large molecular masses. We all know how the presence of phosphoric pentoxide enables tungstic acid to form much larger complexes. Is it not possible that pure thoria does not form large molecules, but that the presence of small quantities of some of the other oxides leads to the formation of the big complex molecule, which transforms the heat waves, rather than transmitting them?

GUAYULE RUBBER. I.

By Theodore Whittelsey.

Received January 22, 1909.

It as long been known that the natives of Mexico in some of their games use balls composed of an elastic substance which they obtain by chewing the bark of a shrub called Guayule. Attempts have been made from time to time to introduce this substance industrially, but without success until recently. The first practical experimentation on a commercial scale seems to have been made in 1903–4. In the following year the product, which has been found to be a true rubber, began to be put on the market. From this time on the industry developed with extraordinary rapidity, and the excitement in northern Mexico is said to have been

comparable to that in Texas when the oil fields were discovered. By 1906 practically all the Guayule within reach of existing transportation facilities was contracted for.

The Guayule, *Parthenium argentatum*, is found on the semi-arid lands of the plateau of northern Mexico, growing in the dry, rocky soil of the foot-hills. It is not large; the dimensions of plants of factory size are approximately as follows:

Height.	Dry weight.	Diameter at base of trunk
12 inches.	6 ounces.	7/8 inches.
20 "	12 "	1 1/8 "
36 "	32 "	2 1/4 "

The average weight of factory shrub is probably between 12 and 16 ounces. The plant shown in the cut is an exceptionally large one, weighing 5¾ lbs. It was 44½ inches high and 2¼ inches in diameter at the ground level.

The shrub is collected by pulling up the entire plant, and is pressed either in the field or at the railway station into bales weighing from 80 to 120 kilos. In 1904 these are said to have brought 7 pesos per ton; in 1905 the price had risen to 30 or 40 pesos and recently has been above 100 pesos (1 peso = $0.50 gold).

Guayule.[1]

The Guayule contains in the neighborhood of 9 per cent. of pure rubber, calculated to the perfectly dry plant. The methods that may be used to extract the crude rubber are entirely different from those used with most rubber plants. These contain a milky juice or latex from which the

Guayule in the field.

rubber is obtained by coagulation, while in the Guayule the rubber exists as such preformed in the plant. The earlier processes were of three types: (1) the alkali process, in which the shrub was boiled with a solution of caustic alkali; (2) the solution processes in which the rubber was extracted by carbon bisulphide or some other solvent; and (3) the mechanical process. The first of these is still used in apparently only one factory. According to the patent specifications, the ground shrub is boiled with three times its weight of 6 per cent. caustic soda for six hours, after which the rubber is skimmed off and freed from alkali. Of the second class, the carbon bisulphide method has been abandoned, because of the expense and the belief that rubber when recovered from a solvent does not possess certain desirable physical qualities to the same degree as an undissolved rubber. A process that belongs to this type has been extensively experimented with in a new factory during the past two years. This process is said to be based on the extraction of the dried shrub with benzol. A solution of rubber and resin is obtained from which the former is precipitated by the addition of alcohol. It has been prophesied that this process will prove a failure for the same reasons that have led to the abandonment of the bisulphide extraction, but the product is now on the New York market and the outcome is awaited with interest. Rubber produced in this

[1] These photographs are kindly furnished by Professor Francis E. Lloyd.

way should run lower in resin than that obtained directly by the other processes. The great bulk of the Guayule rubber now coming into the market is obtained by the third, the mechanical process. In this the shrub is crushed and then ground with water in pebble-mills. The rubber in the plant then becomes apparent as small particles 1/16 inch in diameter and from 1/16 to 1/8 inch long. The details of the succeeding operations to separate the rubber from the woody matter are for the most part kept secret and doubtless vary in different factories, but it may be said in a general way that the procedure is based on the fact that when soaked with water the woody fiber becomes water-logged and sinks while the rubber being lighter than water floats on the surface of the tanks and is skimmed off. It is then washed, sheeted on steel rolls, and either shipped moist or first dried by hanging the sheets in an airy room or by heating gently in a vacuum. If the mechanical process is properly conducted, a practically complete extraction of the rubber from the shrub is secured.

Guayule rubber obtained by the mechanical process is black on the surface when it reaches the market, but olive to light brown within. The dry crude rubber contains about 20 per cent. resin. Some factories also produce a brand from which the resin has been in great part extracted, but the demand for this seems comparatively small. Guayule rubber softens more quickly on the rolls than most other rubbers and therefore requires to be handled somewhat differently, but once this is understood, the working of Guayule rubber of good quality presents no difficulty. It can be substituted for many of the African rubbers, is used to advantage in boots and shoes and many other lines of manufacturing, and seems to be growing in favor. The Guayule rubber recently reported as received at the port of New York was, September 850,000 lbs., October 929,500 lbs., November 1,444,000 lbs.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILL.

GUAYULE RUBBER. II.

DISTRIBUTION OF RUBBER IN DIFFERENT PARTS OF THE SHRUB.

By THEODORE WHITTELSEY.

Received January 24, 1909.

It is generally known to producers of Guayule rubber that more rubber is obtained from the bark of the shrub than from the wood. Apparently the only published statement on the point is in a paper by Endlich[1] in which he says that the ratio of the rubber found in the bark to that found in the wood is approximately 7 to 2. No analyses are given.

In connection with a study of the chemistry of Guayule, the question of the distribution of rubber in the different parts of the plant has been taken up. The results have turned out to be unexpectedly interesting, and to present problems of technical importance.

The material consisted of air-dried plants of different size, selected so as to represent approximately the ordinary run of factory shrub, *viz.*,

	Height.	Weight.	Trunk.	Root.	Branches and leaves.
1 Large plant...	3 ft.	944 g.	165 g.	125 g.	654 g.
2 Medium plants	2½ ft.	747 g.	165 g.	132 g.	450 g.
5 Small plants	2 ft.	2101 g.	637 g.	272 g.	1192 g.
Totals......		3792 g.	967 g.	529 g.	2296 g.

In the division of material the main stem up to the point where its diameter was that of its largest branch was called trunk. The largest branches were less than one-half inch in diameter. The plants had lost most of the leaves in shipment, as is usual, so that the value for "branches and leaves" is practically that of the branches. The trunks and roots were sawed into short pieces (the loss by sawdust amounted to 22 grams in the trunks, 29 grams in the roots) and then steamed until the bark could easily be removed from the wood. A small amount of water-soluble matter was undoubtedly removed in consequence of the steaming, but determinations of water-extractable matter in the whole trunk and in the steamed bark and wood showed that this was negligible. The separate parts were then crushed between steel rolls, dried in vacuum at low temperature, and ground as fine as possible in a coffee mill. The rubber in the bark renders it exceedingly difficult to obtain the material in sufficiently finely divided condition for proper sampling. Many of the particles of bark after the above treatment measured as much as 3 mm. across. This lack of homogeneity manifests itself in the analyses.

Material.	Dry weight.
Trunk bark	349 g.
Root bark	127 g.
Branches and leaves	1918 g.
Trunk wood	404 g.
Root wood	255 g.

The materials were reduced to convenient quantity by careful quartering. The portion taken for analysis was dried to constant weight in a steam-

[1] *Der Tropenpflanzer*, **9**, 233 (1905); *India Rubber World*, **32**, 335 (1905).

oven, and then extracted by boiling successively with water and alcohol. It was dried again to constant weight, and the rubber extracted by boiling with carbon tetrachloride. An aliquot portion of this extract was heated on the steam-bath to remove the solvent, and from the dried residue remaining, the small amount of resin present was removed by boiling successively with acetone and alcohol. The residual rubber was then dried in the steam oven for one hour and a quarter and weighed.

Material.	Per cent. rubber.						
Trunk bark	21.2	21.1	22.7	21.8	19.6	22.9	....
	22.2	19.7	21.4	20.3	22.4		Av. 21.4
Root bark	....	....	....	....	....	19.2	19.8
Branches and leaves	....	....	....	....	....	10.4	9.1
Trunk wood	....	....	....	....	....	0.04	
Root wood	....	....	....	....	....	2.2	1.8

The duplicates vary more than is desirable but an extended series of analyses, made in different ways in the course of development of the method of analysis, showed that better agreement could not be expected from as coarsely divided material as this necessarily was.

These results are at variance with the prevailing belief based in part on Endlich's statement quoted above and in part on early analyses giving 11–15 per cent. rubber in the bark and 2–4 per cent. rubber in the wood. In the single determination of rubber in the trunk wood (0.04 per cent.), the sample, through an interruption of the work, was digested with alcohol for several days. Two other portions of the same material which had been boiled with alcohol for three hours only, as was done with the bark, gave rubber 4.7 per cent.; 4.8 per cent.; but in these the residue weighed as rubber was distinctly abnormal. While elastic, it was brownish red and could not be dissolved with carbon tetrachloride. It seemed probable that the wood contained a substance, not present in the bark, which was not extracted by ordinary treatment with alcohol. To ascertain whether this was the case, new material was prepared. A large plant was collected which consisted of eight branches, each about ¾ inch in diameter, springing almost directly from the root. The first five or six inches of these were steamed and the bark completely removed. Where the bark was ingrowing about knots, not only the bark, but the surrounding wood as well, was cut out. After drying, the wood was then sawed up and the sawdust passed through a 10-mesh sieve which held back only a few chips. The material proved to be of sufficient fineness to allow complete extraction of alcohol-soluble matter in three hours' boiling. After drying to constant weight the wood was then extracted with carbon tetrachloride as usual. Analyses:

Material.	Per cent. rubber.						
Trunk wood	0.06	0.00	0.06	0.13	0.12	0.07	0.07

The appearance of the slight residues here weighed as rubber showed that they were due merely to traces of unextracted wood-resin. This conclusively proved the trunk wood to contain no rubber. The work also showed how the erroneous statements to the contrary have arisen. When the alcoholic extract from the wood was dried, it bore no resemblance to the resinous matter similarly obtained from the bark. The wood-resin is a reddish-brown substance, not at all sticky, and distinctly elastic. After it has been dried in the steam oven it does not dissolve in alcohol, acetone or carbon tetrachloride. It can, however, be extracted from the shrub by tetrachloride. It has sometimes been the custom hitherto to determine the rubber in shrub by extracting directly with tetrachloride, evaporating the solution to dryness and then extracting the residue remaining with alcohol and acetone to remove resins, the undissolved portion being considered to be rubber. Such a procedure applied to the wood would cause this wood-resin to masquerade as rubber, and its elastic nature would contribute to the deception. A study of the resins of the wood and the bark has been begun and will be reported on in a subsequent paper.

The establishment of the fact that the trunk wood contains no rubber rendered it probable that the figures for rubber in the root wood were also due to incomplete extraction with alcohol. Five well-formed roots were therefore selected and the rootlets, ingrowing bark, and dead wood removed. The material remaining was dried and crushed on smooth steel rolls until it was finer than the sawdust used above. Analyses: Rubber, 2.6 per cent.; 2.9 per cent. Although the "rubber-residues" seemed normal, the presence of rubber in the root wood seems so remarkable, in view of its absence from the trunk wood, that the root wood will be further examined. It is possible that it contains a resin comparable in some of its physical properties to the remarkable resin of the trunk wood, but insoluble in alcohol. The root wood will be extracted with acetone in the hope of throwing some light on the question.

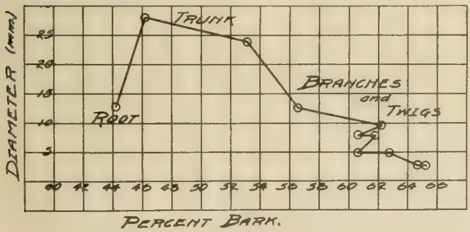
The results given above make it possible to calculate the amount of rubber contained in different parts of the Guayule.

	Dry weight. Gram.	Rubber. Per cent.	Weight of rubber. Gram.	Rubber, parts per 100.
Trunk bark........	349	21.4	74.7	25.7
Root bark.........	127	19.5	24.8	8.5
Branches and leaves	1918	9.7	186.0	64.0
Trunk wood........	404	0.0	0.0	0.0
Root wood.........	255	2.0	5.1	1.7
Totals.........	3053		290.6	99.9

The percentage of pure rubber in the whole trunk is 9.9, the whole root 7.8, the branches and leaves 9.7, and in the whole plant 9.5. These figures are based on perfectly dry material. If the "mill-weight" is taken as a basis (3792 grams — 51 grams (sawdust) = 3741 grams), the percentage of pure rubber in the whole plant is 7.8, which corresponds very closely to published figures[1] and to factory experience. When it is considered that these values for the whole plant are based on analyses of the different parts, varying in rubber content from zero to over 20 per cent., this furnishes substantial confirmation of their essential accuracy.

RATIO OF BARK TO WOOD IN GUAYULE.

Now that it has been definitely established that the trunk wood of Guayule contains no rubber the question of the ratio of bark to wood in the plant acquires importance. Inspection of the material prepared for analysis shows that the trunks of the shrub are made up of 46.4 per cent. bark and 53.6 per cent. wood. To ascertain the per cent. of bark in trunks, branches, and twigs of varying diameter, two-inch sections of such

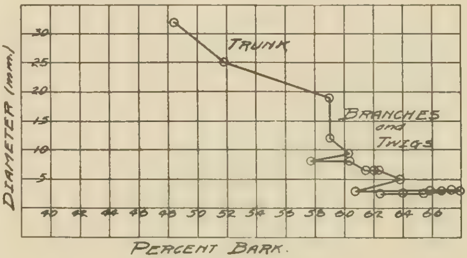


Plant No. 2.

material were accordingly made, steamed, the bark removed from the wood and the bark and wood of each section dried and weighed. The plants used for this purpose, and the results plotted as curves, are as follows:

[1] *India Rubber World*, **1906**, p. 219.

No.	Height. cm.	Weight. Gram.	Circumference at base of trunk. cm.
2	53	350	11
7	42	342	10



Plant No. 7.

To determine the per cent. of bark in the plant as a whole, two plants, weighing 235 grams and 152 grams, were steamed, debarked separately and the parts dried and weighed. The plants contained 54.6 per cent. and 57.8 per cent. bark respectively. If the mechanical difficulties could be overcome, an efficient decorticating device, therefore, would make it possible to nearly cut in two the amount of raw material handled in the mechanical process without diminishing the yield of rubber.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILL.

THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCKS.

By THOS. S. GLADDING, A.M.

Received January 10, 1909.

There are at the present time three recognized methods for the estimation of iron oxide and alumina in phosphate rocks.

First and oldest is the acetate of ammonia process, where the iron oxide and alumina are precipitated as phosphates in an acetic acid solution by addition of acetate of ammonia. The great objection to this method is the unavoidable dragging down of calcium phosphate along with the iron and alumina phosphates, necessitating one, and even more, re-solutions and reprecipitations, in order to completely eliminate the lime.

Second is the Glaser method in which the lime is first removed by converting into calcium sulphate by means of sulphuric acid with addition of alcohol. After filtering, the alcohol is expelled by evaporation, and the iron and alumina precipitated as phosphates.

The third method, published by myself in 1896, throws out both lime and iron by digesting in hot

caustic potash solution. After filtering, the alumina is precipitated as phosphate of alumina either by acetate of ammonia or by addition of ammonia to neutrality.

I will present here a fourth method in which the lime is thrown out as oxalate of lime in an oxalic acid solution.

After filtering from the oxalate of lime the excess of oxalic acid present is removed by destroying with sulphuric acid. The iron and alumina are then precipitated as phosphates.

This new method has been carefully tested by the use of solutions containing known amounts of iron, of alumina, and lime. Chemically pure iron wire, sheet aluminum, and carbonate of lime were employed to make these solutions. Analyzing such solutions I obtained

	Taken. Gram.	Found. Gram.
Calcium oxide	0.008	0.008
Alumina	0.008	0.0083
Iron oxide	0.0094	0.0094
Calcium oxide	0.200	0.2005

The new method was also tested by analyzing a number of phosphate rocks in comparison with the caustic potash method with results as follows:

	Potash method. Per cent.	Oxalate method. Per cent.
Alumina	4.20	4.24
"	2.70	2.63
"	1.40	1.32
"	1.75	1.67
"	1.49	1.59
"	1.37	1.25
"	3.35	3.35
"	1.79	1.75
"	1.50	1.49
"	1.85	1.95

The new method is carried out in detail as follows: Boil 5 grams of the rock phosphate for one hour in 50 cc. HCl (1 : 1), filter into a 250 cc. flask, add a few cubic centimeters of peroxide of hydrogen solution, boil for a few minutes to oxidize iron and expel oxygen, cool, fill to mark and mix. Take 25 cc. (½ gram), heat to boiling, add ammonia to alkalinity, then HCl till just clear, then 1 gram of oxalate of ammonium in crystals, boil gently for a short time, let settle and filter from precipitated oxalate of lime into a 500 cc. Kjeldahl flask, add 5 cc. concentrated sulphuric acid, evaporate to white fumes to destroy excess of oxalic acid. (This boiling down and destruction of oxalic acid can be done in twenty minutes.) Cool, add 50 cc. water, 5 cc. strong HCl, and boil gently a few moments to dissolve any dehydrated sulphate of iron, boiling until solution is clear. Rinse into beaker, make up to about 150 cc. and precipitate the iron and alumina as phosphates either by adding ammonia to neutrality using methyl orange as an indicator, or by making the solution just alkaline with ammonia, just clearing with hydrochloric acid and then adding 25 cc. of acetate of ammonia solution (sp. gr. 1.04). Filter and wash the precipitated phosphates with a boiling hot nitrate of ammonia solution (2½ per cent.). Ignite and weigh, deduct the iron phosphate present and multiply the remainder by 0.418 to obtain the alumina.

The iron oxide is determined by taking 50 cc. (1 gram) of the rock phosphate solution and titrating by either bichromate of potash solution or permanganate of potash solution.

Laboratory of Stillwell Gladding,
New York.

THE ANALYSIS OF COMMERCIAL ACETATE OF LIME.

By Thomas S. Gladding, A.M.

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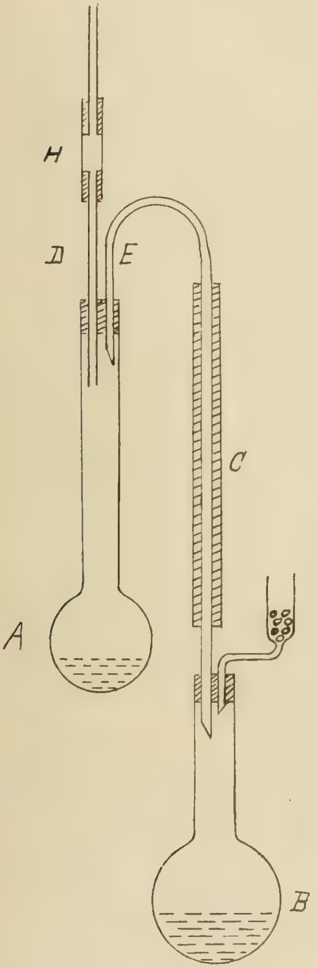
The exporting of commercial acetate of lime assumed noticeable proportions about the year 1890. In the early part of 1902 the exporters abandoned the so-called "English Commercial Test" and called for the estimation of acetic acid by distillation. For some time we used a process where the acetic acid was distilled with an excess of phosphoric acid, the distillation being assisted by a current of steam constantly blown through the body of the distilling liquor. This process was more complex than a simple distillation and great care had to be exercised against a dangerous tendency to carry over phosphoric acid. The constant tendency toward high results led to our abandoning this method, in favor of a new process, devised by myself in 1902. In this new process the use of a current of steam was abandoned for what I may call a "Continuous Constant-Volume Distillation." The method by which this is accomplished is the original feature of this process and is illustrated by the accompanying figure. The distillation flask *A* is closed with a double perforated rubber stopper. The tube *E* connects with the condenser *C*. The tube *D* connects with a reservoir, containing water free from carbonic acid. A screw pinch-cock at *H* regulates the flow of water, allowing it to enter drop by drop and maintaining the contents of the flask at a constant volume.

In this new process two grams of acetate of lime are introduced into a Kjeldahl flask *A* (about

300 cc. capacity) with 30 cc. water. Ten cc. phosphoric acid solution, sp. gr. 170, are added, the contents of the flask are boiled gently for about one and one-half hours while the volume is kept at 50 cc. The distillate passes over through tube



E, is condensed in condenser *C* and received in flask *B* which contains 30 cc. standard alkali solution. At the end of one and one-half hours the contents of the flask *B* are titrated. The distillation is continued until the distillate comes over neutral. Phenolphthalein is used as an indicator. A blank experiment is run and the small amount of acidity obtained in this blank is deducted from each subsequent analysis.

In the *Zeitschrift für analytische Chemie*, **1908**, p. 597, there has been published by W. Fresenius and L. Grünhut, a paper comparing the different methods for the estimation of acetic acid in crude acetate of lime, by distillation with phosphoric acid. The authors make a study of four methods, first that of R. Fresenius, second that of the Color Works of F. Bayer & Co., Elberfeld, third that of K. R. Haberland, and fourth the continuous method devised by myself. They condemn all the methods excepting the second, asserting that they give results too high. They attribute the excessive amount of volatile acid obtained, to a decomposition of the organic constituents of the acetate of lime and the formation of butyric acid. This decomposition they claim is due to too great a concentration of the distillant.[1]

This present paper will interest itself only in their criticism of my method. They speak of it in the following words: "We must reach the conclusion that the errors we find in the R. Fresenius method are not excluded." "We cannot recommend the working of this method." "The analyses show a tendency to go upward."

In answering these criticisms I call special attention to one important matter. The two novel features of my method are first the constant volume of the distillant, about 50 cc. when using 2 grams of acetate; and second the abandonment of a current of steam and the substitution therefor of the addition of water drop by drop. They state that in testing this method they maintained the volume at about 50 cc. but in one case they used 5 grams to 50 cc. and in another 2 grams to 50 cc. It is evident that when they used 5 grams to 50 cc. they were not using my method. Again, and far more important, they say that in both cases they employed a "current of steam," instead of adding water slowly to the distillant. It is evident therefore, that in none of their work did they really use my method and that their results have no value whatever as a criticism of the accuracy of my method.

The authors speak of testing the method by a "series" of tests. This "series" consists of four

[1] A newly coined word, to express the contents of the distilling flask. It is derived from the present participle distillans (the thing distilling) as distillate is derived from the past perfect participle distillatus (the thing distilled).

analyses of a brown acetate of lime. They also fail to carefully follow the method in its most essential feature, namely, the slow addition of water as a substitute for a current of steam.

To ascertain whether the objections urged by the authors, are of any value as applied to my method, when correctly carried out, I have made a number of analyses, using widely varying degrees of concentration. Thus I have taken 5 grams of acetate of lime, added 25 cc. water and 25 cc. phosphoric acid solution sp. gr. 1.70, distilled to a volume of 30 cc. and continued the distillation for two hours, till no further volatile acid could be obtained. At the same time, 2 grams acetate plus 10 cc. phosphoric acid solution were distilled at a volume of 40 cc. for two hours, also 1 gram acetate plus 5 cc. phosphoric acid solution was distilled at a constant volume of 50 cc. for two hours, till all volatile acids were over. These three experiments were made with a brown acetate of lime, also with a gray acetate of lime. The results were as follows:

Brown Acetate of Lime.

One g. + 5 cc. phos. acid sol. at constant vol. of 50 cc. gave 67.80%.
Two g. + 10 cc. phos. acid sol. at constant vol. of 40 cc. gave 67.75%.
Five g. + 25 cc. phos. acid sol. at constant vol. of 30 cc. gave 67.90%.

Gray Acetate of Lime.

One g. + 5 cc. phos. acid sol. at constant vol. of 50 cc. gave 83.57%.
Two g. + 10 cc. phos. acid sol. at constant vol. of 40 cc. gave 83.41%.
Five g. + 25 cc. phos. acid sol. at constant vol. of 30 cc. gave 83.41%.

We notice in these experiments that although the concentration, when using 5 grams, is ten times that when using 1 gram, nevertheless, no more volatile acid is obtained from the greater degree of concentration.

I tested the question still more rigorously and conclusively, by taking the residue of the 5 grams distillant. After expelling all volatile acid, I added 50 cc. water and 1 gram C. P. acetate of soda. I obtained after exhaustive and continued distillation 100.1 per cent. of acetate of soda.

I consider that the above work completely vindicates the method as proposed by myself. I also express the opinion that the high results obtained by Fresenius and Grünhut are due to the use of a current of steam. The experience of Grosvenor is similar to my own. He says:[1] "Steam should never be used for distillation." As has been stated in an earlier part of this paper, I abandoned the use of a steam current because of its tendency to give results higher than the truth.

Laboratory of Stillwell & Gladding.

[1] *Jour. Soc. Chem. Ind.*, **1904**, p. 535.

THE RAPID DETERMINATION OF MOISTURE IN COMMERCIAL PRODUCTS OF A VISCOUS OR SEMI-SOLID CONSISTENCY.[1]

By Arthur Lowenstein.

Received January 16, 1909.

The object of this investigation was to secure a rapid method for the determination of moisture in concentrated solutions of a viscous or semi-solid consistency, such as are frequently encountered in a modern packing-house. Later the method was extended to other products having similar physical characteristics. In the case of some products, such as meat extracts, it is frequently desirable and necessary to secure a rapid determination of the moisture content of the product, in order not to delay the process of manufacture. In many laboratories in order to facilitate matters, such moisture determinations are conducted by allowing the material to dry in an oven over night. Such prolonged heating of organic nitrogenous material, however, is frequently conducive to chemical decomposition, and the results of the determination are often high. The present methods for the direct determination of moisture in such products as are under discussion, usually consist in drying a definite quantity of the material to a constant weight at a specified temperature (usually that of boiling water, or 105° C.) either by itself or with the admixture of ignited asbestos, pumice stone, quartz sand, or some similar material. In this way the moisture is determined in from 5–24 hours, depending upon the nature of the product. When the longer period is required, such as in the case of molasses and fruit jellies, etc., some decomposition is very apt to occur.

The method herein employed consists merely in the application of several well-known principles, *viz.*, the addition of a dehydrating agent, of a lower boiling point than water, in which the material to be desiccated is wholly or in part soluble, or at least miscible. The reagent employed was ethyl alcohol, and for the sake of economy, the ordinary 95 per cent. alcohol (by volume) was used. In the case of materials containing proteins in solution, the alcohol also acts as a coagulant in some cases, and as a precipitant in others, which action facilitates the drying process. The method employed consists in weighing a small quantity of the sample in a metal dish, 2½ inches in diameter (the metal

[1] Read before the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society at Baltimore, Dec. 29, 1908.

caps such as used on meat extract jars answer very well) together with a short glass stirring rod flattened at one end to facilitate spreading the material uniformly over the surface of the dish. About 15 cc. of the alcohol are added and thoroughly incorporated with the sample. The dish is then placed on the steam bath and the alcohol evaporated, with frequent stirring; another portion of 15 cc. are then added and evaporated in a similar manner. In case of materials which are very difficult to dry, four applications of alcohol will be found advantageous—or one or two applications of absolute alcohol are particularly effective. Drying is continued on the steam bath for thirty minutes, then the dish is transferred to a double-walled oven and heated to constant weight at 105°

Alcohol has been used for years in the determination of moisture in soap, which product is soluble in this solvent. The author, however, is not aware of its employment for this determination in food products, or others of the nature herein mentioned.

The appended table will give some idea as to the accuracy and usefulness of the method. Its use can no doubt be extended to many commercial products not mentioned herein. It is necessary to bear in mind that it is difficult to obtain uniform samples of some of these products and therefore the results in some cases can at best only be approximate. In all cases I think it is safe to assume that the shorter the period of drying, at moderate temperatures, the less likelihood there is of decomposition of the product.

Lab. No.	Description of samples.	Wt. of portn. Gms.	Dried on steam bath.	Dried in oven 105° C.	Dried to constant weight hrs.-min.	Per cent. H_2O.	Remarks.
38000	Extract of beef. Low salt—3.5% NaCl	2.00	30 min.	1 hr.	1–30	28.70	2 port. 15 cc. ea. alcohol
38001	Extract of beef. High salt—18% NaCl	2.01	30 min.	1 hr.	1–30	24.01	2 port. 15 cc. ea. alcohol
38002	Concentrated glue sol.—"Glue jelly"	2.04	30 min.	2 hrs.	2–30	61.35	2 port. 15 cc. ea. alcohol
38003	Concentrated tank water—"stick"	2.01	30 min.	1 hr.	1–30	50.25	2 port. 15 cc. ea. alcohol
38003	Concentrated tank water—"stick"	2.00	30 min.	2 hrs.	2–30	50.01	2 port. 15 alcohol, 1 gr. asbestos
38004	Inspissated ox gall	2.03	30 min.	1 hr.	1–30	38.29	2 port. 15 cc. alcohol
38004	Inspissated ox gall	2.00	....	6 hrs.	6	38.24	No alcohol used
38004	Inspissated ox gall	2.00	....	17 hrs.	17	38.55	Dried overnight
38005	Dyewoods—Fustic extract	2.01	30 min.	2 hrs.	2–30	48.42	2 port. 15 cc. alcohol
38005(a)	Dyewoods—Logwood extract	1.30	30 min.	3 hrs.	2–30	43.10	Heated 5 min. on steambath before adding alcohol
38006	"Cane and maple" syrup	2.09	30 min.	4 hrs.	4–30	35.00	2 port. 15 cc. alcohol
38006	"Cane and maple" syrup	1.03	30 min.	2 hrs.	2–30	35.13	2 port. 15 cc. alcohol
38006	"Cane and maple" syrup	2.09	....	17 hrs	17	35.44	Overnight no alcohol
38007	Cottage cheese	2.03	30 min.	2 hrs.	2–30	76.99	2 port. 15 cc. alcohol
38007	Cottage cheese	3.00	10 hrs.	...	10 hrs.	76.97	Official A. O. A. C. method
38007	Cottage cheese	2.04	....	17 hrs.	17	76.57	Overnight, no alcohol
38008	Neufchatel cheese	2.02	30 min.	2 hrs.	2–30	73.51	2 port. 15 cc. alcohol
38008	Neufchatel cheese	3.00	10 hrs.	...	10	73.36	Official A. O. A. C. method
38008	Neufchatel cheese	2.11	....	17 hrs.	17	74.07	Overnight no alcohol
38009	Philadelphia cream cheese	2.01	30 min.	2 hrs.	2–30	35.62	2 port. of alcohol
38009	Philadelphia cream cheese	2.01	30 min.	2 hrs.	2–30	35.27	2 port. of alcohol, asbestos added
38009	Philadelphia cream cheese	3.01	10 hrs.	...	10	35.12	Official A. O. A. C. method
38010	American cheese	2.00	30 min.	2 hrs.	2–30	41.49	2 port. of alcohol
38010	American cheese	2.01	30 min.	2 hrs.	2–30	41.46	2 port. of alcohol, asbestos added
38010	American cheese	3.09	10 hrs.	...	10	41.58	Official A. O. A. C. method
38011	Molasses	1.00	30 min.	7 hrs.	7–30	30.01	No alcohol, 30 gr. quartz sand—Horne's method
38011	Molasses	1.00	30 min.	5 hrs.	5–30	29.86	Horne's method plus 2 port. alcohol
38011	Molasses	1.00	30 min.	6 hrs.	6–30	29.75	45 gr. lead shot, 2 port. alcohol

C. In the case of most substances under consideration, the total period of drying is from one hour and thirty minutes to two hours and thirty minutes. Some materials require a longer time, but in practically all cases the above treatment will materially shorten the time of drying. In some instances the use of ignited asbestos, or mineral wool as an absorbent was of value, but not as a general rule. With molasses and fruit jellies, lead shot proved to be quite effective in increasing the heating surface. The use of a good conductor of heat, such as the lead shot, has some advantage over poor conductors, like quartz sand.

The author desires to express his appreciation of the assistance rendered in this work by Edward Moore and William P. Dunne.

Chemical Department,
Morris & Company,
Chicago, Ill.

A NEW METHOD FOR THE CALCULATION OF THE PROTEINS IN MILK.

By Geo. A. Olson.

In the year 1906 the formula (protein = 0.368 total solids + 0.33 ash — 0.383 fat) for the calculation of protein in milk devised by the writer was

published in the Proceedings A. O. A. C.[1] Since that time the writer has derived a simpler formula which will be discussed in this paper.

In studying the composition of milk from individuals of the same or different breeds of cows it has been found that the ratio of the fat to the protein or casein may vary.[2] A divergence in this respect, however, is generally accompanied by a variation in the specific gravity, since the specific gravity of a milk differs according to the relative amounts of the components present.

It frequently occurs that different milks contain the same amount of fat and yet the solids-not-fat of such milk may vary quite widely. With equal fat content, the milk containing the highest or lowest total solids or solids-not-fat will also have the highest or lowest specific gravity, respectively. Again milks having equal total solids will vary in their specific gravities according to the amount of fat present; the milk having the highest fat content will have the lowest specific gravity. A closer scrutiny of the composition of milk also reveals these facts: *First*, milk which has a high fat content also has a high protein content; *second*, milk which has a high specific gravity has also a high protein content and milk which has a low specific gravity has accordingly a low protein content, providing the fat content in such milks are equal. These facts are clearly brought out in the following table.

TABLE I.—INFLUENCE OF SPECIFIC GRAVITY ON PROTEIN CONTENT OF MILK.

No.	Specific gravity.	Total solids. Per cent.	Fat. Per cent.	Protein. Per cent.
1	1.0361	14.08	4.40	3.69
2	1.0288	12.56	4.40	3.11
3	1.0394	13.91	3.30	3.84
4	1.0300	11.23	3.30	2.99
5	1.0352	15.15	5.28	4.12
6	1.0311	15.16	6.25	3.69

The first two samples of milk given in Table I have equal fat content but differ in their specific gravities, total solids and protein contents. Likewise the same is true for numbers 3 and 4. Number 3, however, was an abnormal milk and is given in order to show how a milk of high specific gravity can also have a high protein content. Numbers 5 and 6 have equal total solids, but differ in their specific gravities, fat and protein contents.

Instead of taking into account milk of average composition, we may consider the composition of milk from cows of any breed. The milk from a Holstein cow tested 3.3 per cent. fat, the total solids was 11.8 per cent. and contained 3.12 per cent. protein, the milk from a Jersey cow tested 4.55 per cent. of fat with a total solids of 13.5 per cent. and contained 3.28 per cent. protein. The ratio of fat to protein in the former case is 1:0.95 while in the latter it is found to be 1:0.72. In this illustration the proteins are practically the same while the fat content of the two milks differs by 1.25 per cent. Considering, however, the total solids of the two milks in the above illustration and determining the ratio of solids-not-protein to the total solids gives a ratio for the Holstein cow of 1:1.358 and 1:1.320 for the Jersey. In other examples the ratio of solids-not-protein to total solids varies for the above types and other breeds, indicating that this ratio is independent of breed characteristics. Instead of taking the average ratio of a large number of analyses the writer chose 1.34 as the number, because this figure represents the specific gravity of milk protein.

By the use of the number 1.34 the protein can be readily calculated for average purposes, particularly where herd milk is considered and even in the case of individuals in normal health, when the total solids of the milk are known. To illustrate, the total solids are divided by 1.34 and the quotient thus found, representing the solids-not-protein, is subtracted from the total solids, the difference representing the per cent. of protein in a given milk.

The extreme variations of the ratio of solids-not-protein to total solids found in all normal milks analyzed by the writer did not vary more than 0.084, and this variation was regardless of breed or individual characteristics. The following table shows the extreme variations of the solids-not-protein to total solids of milk comprising four different breeds in the Wisconsin University Dairy Herd. A comparison of the calculated to the actual protein content of these milks is also given.

In Table II it will be noted that there is an extreme variation in the ratio of the solids-not-protien to total solids of 0.084, and the variations are independent of breed; the ratio of fat to protein, on the other hand, ranges from 1:0.59 to 1:0.99, or a difference of 0.40.

The accuracy of a formula for the estimation of protein can best be determined when compared with actual analyses of the protein in milk from individuals of different breeds at different periods of lactation.

[1] *Bull.* **99**, Bur. of Chem., U. S. Dept. of Agri., p. 106.

[2] L. L. Van Slyke, *Jour. Amer. Chem. Soc.*, **30** (1908), No. 7, pp. 1166–1186.

TABLE II.—VARIATIONS OF SOLIDS-NOT-PROTEIN TO TOTAL SOLIDS OF MILK FROM DIFFERENT BREEDS.

Breed.	Solids-not-protein to total solids.	Total solids. Per cent.	Fat. Per cent.	Protein found. Per cent.	Protein calculated. Per cent.	Ratio of fat to protein.
Ayrshire..........	1:1.370	13.42	4.40	3.63	3.40	1:0.83
"	1:1.297	12.72	4.03	2.91	3.22	1:0.72
"	1:1.340	12.56	3.50	3.21	3.19	1:0.92
Jersey	1:1.378	13.67	4.60	3.75	3.47	1:0.82
"	1:1.314	13.29	4.38	3.18	3.38	1:0.72
"	1:1.342	15.03	5.85	3.83	3.82	1:0.65
Guernsey.........	1:1.369	14.32	5.10	3.86	3.63	1:0.76
"	1:1.294	14.35	5.53	3.26	3.64	1:0.59
"	1:1.344	14.28	5.20	3.66	3.63	1:0.76
Holstein	1:1.386	11.32	3.20	3.15	2.87	1:0.99
"	1:1.301	10.40	2.75	2.41	2.64	1:0.88
"	1:1.342	12.73	4.03	3.25	3.23	1:0.81

From the data given in Table III it will be noted that the proteins determined by calculation are fairly concordant with those obtained by the Kjeldahl method. The ratio of fat to protein ranged from 1:0.65 to 1:0.91.

TABLE III.—ACTUAL AND CALCULATED PROTEIN CONTENT OF MILK FROM DIFFERENT BREEDS AT DIFFERENT PERIODS OF LACTATION.

Breed.	Specific gravity.	Total solids. Per cent.	Fat. Per cent.	Protein found. Per cent.	Protein calculated. Per cent.	Ratio of fat to protein.
Holstein, No. 1.....	1.0311	11.25	3.14	2.84	2.86	1:0.90
" " 2.....	1.0322	12.39	3.50	3.35	3.15	1:0.91
" " 3.....	1.0303	10.61	2.90	2.53	2.69	1:0.87
Ayrshire, " 1.....	1.0330	12.77	3.88	3.29	3.24	1:0.85
" " 2.....	1.0323	12.52	3.90	3.05	3.18	1:0.80
" " 3.....	1.0339	13.10	3.93	3.45	3.32	1:0.88
Jersey, " 1.....	1.0341	14.98	5.68	3.72	3.80	1:0.65
" " 2.....	1.0334	13.23	4.36	3.19	3.36	1:0.73
" " 3.....	1.0348	15.54	6.03	3.96	3.94	1:0.65
Guernsey, No. 1....	1.0336	14.29	5.13	3.64	3.63	1:0.71
" " 2....	1.0340	13.37	4.33	3.30	3.39	1:0.76
" " 3....	1.0331	15.29	5.91	3.87	3.88	1:0.67

The ratio 1:1.34 as stated in the preceding pages has been taken as representing the relation of the solids-not-protein to total solids. Exceptions to this ratio have been found in the case of milk from cows affected with tuberculosis of the udder, mammitis (garget), freshened (colostrum) or strippings, etc. Some of the exceptions to this ratio and the cause for the variations are given in the following table:

TABLE IV.—EXCEPTIONS TO THE RATIO 1:1.34.

Breed.	Specific gravity.	Total solids. Per cent.	Fat. Per cent.	Protein found. Per cent.	Protein calculated. Per cent.	Cause for abnormality. 0.8 lb. milk per milking.
Brown Swiss.	1.0366	16.83	6.10	5.53	4.26	
Guernsey....	1.0330	14.26	5.20	3.09	3.62	Garget
Holstein.....	1.0350	14.50	4.30	4.26	3.68	Rheumatism
"	1.0304	11.19	3.00	3.30	2.84	Garget
"	1.0400	14.06	3.30	5.52	3.57	Colostrum
Ayrshire.....	1.0334	13.89	4.38	4.00	3.53	Garget
"	1.0332	13.75	4.48	4.19	3.50	Colostrum
"	1.0333	13.35	4.00	3.99	3.39	Milk fever
Jersey.......	1.0378	16.02	5.20	5.06	4.06	Garget

The tendency for the composition of milk from individuals to vary is far greater than where the herd milk is considered as a whole. Any abnormality (Table IV) in the composition of milk from a few cows would be reduced by the number of cows in a herd producing normal milk.

It has been shown that the relation of the solids-not-protein to the total solids is very nearly constant in normal milks, therefore the protein must be in direct relation to the total solids. From this it would follow that the sugar plus fat and ash should be in relation to the total solids. Since the ash is practically constant in milk (0.75 per cent.) we may consider only the sugar and fat. The writer found that the ratio of solids-not-fat or solids-not-sugar to the total solids varied within rather wide limits; it follows from this that the sugar and fat do not necessarily stand in a definite relation to one another and consequently the two must be considered together. Accordingly it was found that the sum of these two constituents (fat and sugar) stand in a definite relation to the total solids, and several formulae have been constructed, depending upon whether or not the ash should be considered independent from the other solids. From any one of the formulae given below the protein or sugar can be obtained, and if we consider the ash constant in all milk we have therefore, a method of estimating the amount of protein and sugar in all normal milks when the specific gravity and the fat are known.

1. $(TS)—TS/1.34 \doteq P$.

2. $(TS–A)—TS–A/1.365 = P$.

3. $(TS)—TS/3.25 = F + S + A$, or $(TS)/3.25—A = P$.

4. $(TS–A)TS–A/3.694 = F + S$, or $TS–A/3.694 = P$.

where TS = total solids; P = protein; A = ash; F = fat; and S = sugar.

TABLE V.—THE CORRESPONDING PROTEIN OR CASEIN CONTENT OF MILKS CONTAINING FROM 10.00 TO 16.50 PER CENT. TOTAL SOLIDS.

Total solids. Per cent.	Protein. Per cent.	Casein. Per cent.
10.00	2.54	2.03
0.50	2.66	2.13
11.00	2.79	2.24
0.50	2.92	2.34
12.00	3.04	2.43
0.50	3.17	2.54
13.00	3.30	2.64
0.50	3.42	2.74
14.00	3.55	2.84
0.50	3.68	2.94
15.00	3.80	3.04
0.50	3.93	3.14
16.00	4.06	3.25
0.50	4.19	3.35

The preceding table has been constructed from the formula (TS) — TS/1.34 = P and contains the total solids of milk from 10.00 to 16.50 and its equivalent in protein which runs from 2.54 to 4.19. The casein has been calculated on the assumption that 80 per cent. of the protein is casein.

In the preceding paragraph it was assumed that eighty per cent. of the total protein of milk is casein. Analytical data show the casein to range from 78 to 82 per cent. of the total protein, hence the casein can be calculated by multiplying the per cent. of protein by 0.8. Dr. Van Slyke's figures[1] for protein have been multiplied by 0.8 and compared with the actual results of casein as determined by him. The maximum, minimum and average results of fifty-eight analyses are as follows:

Table VI.—Comparison of Actual and Calculated Casein Content.

	Casein found. Per cent.	Casein calculated. Per cent.	Difference.
Maximum	3.55	3.50	+0.12 to −0.25
Minimum	2.11	2.07	0.00
Average	2.70	2.69	−0.01

The results obtained by calculation and summarized in Table VI are within the limits of error. From this it appears unnecessary to make casein determinations in milk.

CONCLUSIONS.

1. The relation of the solids-not-protein to total solids in different samples of milk is practically constant and may be considered on the average, equal to 1 : 1.34.

2. The protein content of normal milk can be calculated with a fair degree of accuracy when the total solids are known by the formula (TS) — TS/1.34 = P. The per cent. of casein can be found by multiplying the per cent. of protein by 0.8.

(Contribution from the Bureau of Chemistry, U. S. Department of Agriculture.)

THE DETERMINATION OF BENZALDEHYDE IN ALMOND FLAVORING EXTRACT.

By W. Denis and P. B. Dunbar.

Received February 1, 1909.

The methods proposed for the determination of benzaldehyde in flavoring extracts may be divided into three classes:

(1) Methods based on the formation of the addition product with acid sodium sulphite.[2]

(2) Colorimetric methods.[1]

(3) Methods involving the precipitation of the oil of bitter almonds.[2]

In the examination of almond extracts of known composition by these methods, we have found that the sodium hydrogen sulphite method invariably gives results far below the truth, with the colorimetric method we have not been successful, while Howard's precipitation method is apt to give figures much too high, due probably to the difficulty of removing the last traces of chloroform.

We have found that we are able to obtain results within 97 to 99 per cent. of the theory by precipitation of the benzaldehyde in almond extract, and in bitter almond oil, as the phenylhydrazone[3] according to the equation

$$C_6H_5.CHO + NH_2.NH.C_6H_5 \rightleftarrows C_6H_5.CH = N.NHC_6H_5 + H_2O.$$

This method has already been proposed by Denner[4] for the quantitative determination of benzaldehyde in bitter almond water; by Rocques[5] for its determination in kirsch; and by Herissey[6] for the determination of the benzaldehyde resulting from the hydrolysis of amygdalin.

The reagents used by us are:

Reagent (1):	Phenyl hydrazine hydrochloride	2 grams
	Crystals of sodium acetate	3 "
	Water	20 cc.

Dissolve the sodium acetate in the water, add the phenyl hydrazine hydrochloride, shake for five or six minutes, and filter, or

Reagent (2):	Phenyl hydrazine	1 cc.
	Glacial acetic acid	1.5 cc.
	Water	20 cc.

Mix the acetic acid and water, then pour in the phenyl hydrazine.

Reagent (2) we find to be much more convenient on account of the rapidity with which it may be prepared. Whether reagents (1) or (2) be used, the solution should be made up immediately before use, and solutions more than an hour old should be discarded. The method of precipitation is as follows:

Two 10 cc. portions of almond extract are measured into 300 cc. Erlenmeyer flasks; to one portion is added 10 cc., to the other 15 cc. of either reagent; shake, stopper tightly, and allow to stand over night in a dark place. The next day add 200 cc.

[1] *Jour. Amer. Chem. Soc.*, **30** (1908), No. 7, pp. 1169–1174.

[2] U. S. Pharmacopoeia, VIII, p. 68. Leach, Food Inspection and Analysis, p. 750.

[1] Woodman and Lyford, *Jour. Amer. Chem. Soc.*, **30**, 1607.

[2] Howard, *Ibid.*, **30**, 610.

[3] Fischer, *Liebig's Ann. d. Chem.*, **190**, 134.

[4] Denner, *Zeit. für analyt. Chem.*, **29**, 228. *Pharm. Centralhalle*, **28**, 527.

[5] Rocques, *Rev. Internat. des Falsifications*, **1907**, p. 66.

[6] *Journ. de Pharm. et de Chim.*, **1901**, p. 60.

of cold water to each flask, and filter on tared Gooch crucibles provided with thin mats of asbestos. Wash with cold water and finally with 10 cc. of 10 per cent. alcohol. Dry for three hours in a vacuum oven at 70–80° C. If a vacuum oven is not available, the drying may be accomplished in a vacuum desiccator over sulphuric acid, but will of course take much longer than when a higher temperature is employed. The weight of the precipitate, multiplied by 5.408, gives the number of grams of benzaldehyde in 100 cc. of the solution.

Our reason for using 10 and 15 cc. of reagent on different portions of the same extract is based on the fact, that we have found in the examination of a large number of commercial extracts, that while the large majority conform to the official standards,[1] and contain in the neighborhood of 1 per cent. by volume of oil of bitter almonds, occasionally extracts are met with containing as much as 6 per cent. of benzaldehyde; in such preparations it is obvious, that, while the use of 10 cc. of the reagent may give good duplicates the results would be far below the truth.

The following results have been obtained on almond extracts made in this laboratory, and containing known amounts of benzaldehyde or oil of bitter almonds.

Analyst.	Gr. benzaldehyde per 100 cc. in sol.	Gr. bitter almond oil per 100 cc. in sol.	Gr. benz. aldehyde per 100 cc found.	Per cent. benzaldehyde recovered.	Grs. bitter almond oil per 100 cc. found.[2]
E. H. G	0.995	...	0.989	99.5	.
W. E. H.......	0.995	...	0.973	97.8	..
W. D..........	1.659	...	1.600	97.0	
W. D..........	0.995	...	0.966	97.0	..
W. D....	...	1.086	0.949	.	1.090
W. D..........	...	0.947	0.787	..	0.905
P. B. D........	1.00	...	0.980	98.0	...
P. B. D........	...	1.00	0.890	..	1.02

The presence of benzoic acid, which in varying amounts must always be present in almond extracts, does not affect the accuracy of the results.

(*a*) In a solution containing 1.6598 grams of benzaldehyde and 0.610 gram benzoic acid per 100 cc. there was found, on analysis, 1.638 grams benzaldehyde, which is equal to 98 per cent. theory.

(*b*) In a solution containing 1.6598 grams benzaldehyde and 1.220 grams benzoic acid per 100 cc. there was found, on analysis, 1.628 grams benzaldehyde per 100 cc. which is equal to 97 per cent. theory.

[1] Circular 19, Office of the Secretary, U. S. Department of Agriculture.

[2] Oil of bitter almonds calculated from the benzaldehyde by use of the U. S. P. Standard, *i. e.*, that oil of bitter almonds shall contain at least 85 per cent. benzaldehyde.

In the same way it was found that nitrobenzol, which is sometimes placed in almond extracts, has no effect on the precipitation.

(*a*) A solution containing 0.9950 gram benzaldehyde and 0.8676 gram nitrobenzol per 100 cc. gave 0.9756 gram benzaldehyde per 100 cc., which is equal to 98 per cent. of theory.

(*b*) A solution containing 0.5 gram benzaldehyde and 0.5 gram nitrobenzol per 100 cc. gave 0.498 gram benzaldehyde per 100 cc., which is equal to 99.6 per cent. theory.

REVIEW.

PHARMACEUTICAL CHEMISTRY DURING 1908.

Upon comparing the broad and rapid progress made during the last year along the lines of synthetic organic chemistry, with what has been accomplished among the medicinal synthetics, we regret to note that nothing original has appeared. No new fields have been opened; what progress has been made was along the well beaten paths with duplication of old ideas in other forms. The inevitable result of continuing such a multiplication along old lines is to increase confusion and finally compel the medical profession to fall back to their old standard remedies.

Local Anesthetics.

The study of the structure of cocaine, demonstrated that its local anesthetic action resided in two nuclei, namely, a substituted pyridin ring and an esterified benzoic acid. As chief synthetic representatives of the former class were the "Eucaines," along this line, nothing new has developed. Among the older and successful representatives of the latter class, esters of aromatic amino and oxyamino acids, are the ortho forms (oxybenzoic methyl esters) and anesthesin (*p*-amino-benzoic ethyl ester). They are non-toxic and serve especially for anesthesia of the nerve terminals. The objectionable insolubility was overcome through the introduction of an amino-alcohol in place of H of the COOH group as in novocain, a *p*-amino-benzoyl-diethyl-amino ethanol [$C_6H_4(NH_2)COO.C_2H_4N(C_2H_5)_2.HCl$]. The amino-cinnamic alkaline esters (D. R. P. 187,593) are still more powerful local anesthetics. New among this class is Propaesin, the propyl ester of *p*-amino-benzoic acid, m. p. 73 to 74° C. ($NH_2C_6H_4COOC_3H_7$) which, like others of this class, serves as a mild anesthetic adapted to diseases of the esophagus and inflamed mucous surfaces. Dipropaesin, a condensation-product of the former, which splits up into propaesin when in contact with alkalies, serves as a local anesthetic in gastro-intestinal affections. The esterifying group has, of recent years, grown to such proportions and pharmacologic importance, securing thereby more profound anesthesia, that such derivatives may be considered as substituted tertiary alcohols. As prototypes of this class are stovaine, the hydrochloride of dimethyl-amino-benzoyl-dimethyl carbinol [$(C_6H_5CO.O)C(CH_3)(C_2H_5)(CH_2.N(CH_3)_2.HCl$] and alypin, the hydrochloride of benzoyl 1,3-tetra-methyl-diamino-2-ethyl-isopropyl alcohol [$(C_6H_5CO.O)C(C_2H_5)(CH_2.N(CH_3)_2)_2HCl$]. The success attending the introduction of these led to a number of recent patents along similar

lines. Among such are benzoyl derivatives of alkyl amino-ethanols and alkyl amino-pentanols, E. Schering, D. R. P. 175,080, 181,287; alkamin esters of benzoic and salicylic acids, Hoechst Co., D. R. P. 187,209, 188,571; benzoyl derivatives of tertiary amino alcohols in which acid radicals enter into the amino and hydroxyl groups, J. D. Riedel Co., D. R. P. 189,481, 183,361; amino-ethers of primary alcohols through interaction between halogen derivatives of alkyl ethers of the hydrocarbons ($CH_2X.OR$) and amines, D. R. P. 184,968, also products of action of chlorin derivatives of the general formula $RRN.CH_2.CH_2Cl$ on *p*-amino-benzoates, D. R. P. 189,335, E. Merck.

The allied field of suprarenal active principles, which are largely employed in conjunction with local anesthetics, has become one of the most important in modern medicine. Nowhere in the domain of medicinal synthetics has organic chemistry exhibited greater triumphs in duplicating Nature's products. Among the older preparations are adrenalin, adnephrin, suprarenalin, adrenal, epinephrin, hemisine, etc., which represent active extracts of the glands or synthetic products. New additions are suprarenin, methyl-amino-ethanol-pyrocatechin $[(OH_2).C_6H_3.CHOH.CH_2.NH(CH_3).HCl]$; Homorenon, amino-ethyl-amino-aceto-pyrocatechin $[(OH)_2 C_6H_3.CO.CH_2.NH.C_2H_5.HCl]$ and Arterenol, amino-ethanol-pyrocatechin $[C_6H(OH)_2.CHOH.CH_2.NH_2.HCl]$.

Antiseptics and Disinfectants.

This field has been so thoroughly worked over during the last decade that the market has become flooded and physicians bewildered by the immense number and variety of products. No new fields have been opened, hence progress in this direction has been in amplifying old ideas. *Formaldehyde Preparations:* Dr. M. Goldschmidt (D. R. P. 183,856) offers a new method for preparing formaldehyde from metallic formates through the action of CO of furnace gases on oxides. For the disinfection of rooms, autan has not been surpassed, The only addition to the almost innumerable condensation products of formaldehyde (used as dry antiseptics) is Decilan, a formaldehyde potassium oleate. The valuable antiseptic *Silver Combinations* which can scarcely be improved upon, is enriched by Argoferment, a soluble colloidal silver, similar to v. Heyden's Collargol. More important among the miscellaneous antiseptics are Paralysol, a solid cresol ($C_6H_4CH_3OK.3C_6H_4(CH_3)OH$, m. p. 146°); Boryl, ethyl borosalicylate; Nizin, a zinc sulfanilate; Chrysyl, a zinc boropicrate; Griserin New, claimed to be an isomer of loretin (iodo-oxyquinolin-sulphonic acid, D. R. P. 187,869). Aminosol, a pure oxyquinolin sulphate (D. R. P. 187,943), 25% more active than the older impure product, has appeared. Noteworthy is the increase in the use of colloidal sulphur, introduced by v. Heyden under the name of Sulfoid (D. R. P. 164,664) prepared by precipitating sulphur in presence of such colloids as albumin in acid solution.

Intestinal and Urinary Antiseptics.

The ever-increasing number of organic combinations of bismuth, which aim to serve as local antiseptic desiccants or intestinal antiseptics, has received the largest number of additions. Among these are Neoforma, a basic triodo-phenol bismuth ($C_6H_2I_3O.BiO$); Helkomen, a basic dibrom-β-oxy-naphthoate ($C_8H_6Br_2.COO.BiO.CO.BiO$); Biscinoid, a bismuth cinchonin iodide; Gastrosan, bismuth bisalicylate; Iodomenin, iodo bismuth albuminate, and Radiovis, a radio-active bismuth subnitrate, specially intended as an intestinal disinfectant. Investigations have demonstrated that thorough intestinal asepsis is not attainable; theoretical possibilities have not been borne out in practice. Substances which possess, in general, superior antiseptic properties and have shown themselves to be useful in disinfection of the stomach, utterly fail to stop fermentation in the intestinal canal. This is due to the alkalinity of the intestinal secretions, which in many cases renders the antiseptic useless. One class of chemicals best adapted for this purpose, are such condensation-products which, because of their insolubility, reach the lower intestines, then slowly break up with liberation of their medicinal constituents. To this class belong such condensation-products of formaldehyde and tannin as Tannopin, Tannocasum and Tannoform and various esters of tannin, Tannosal, Tannogen, Tannochrom, etc. New are Tannothymal (D. R. P. 188,318), a condensation-product of formaldehyde, thymol and tannin; Tannyl, a tannin compound of oxychlor-casein; Tannin Silver Albuminate, a combination of albumin, tannin and silver; Fixin, an aluminum lactate. There are but few additions to the many and useful derivatives of hexamethylene tetramine which serve as disinfectants in treatment of diseases of the urinary organs and tract. Prominent among these are Silin, a hexamethylene citrosalicylate and Dorovertin (D. R. P. 188,815), a borate of urotropin.

Hypnotics and Sedatives.

The various hypnotics that belong to the different classes of organic compounds, exemplified by chloral, urethane, paraldehyde, amylene hydrate, sulfonal, trional, chloral formamid, dormiol and hedonal (methyl-propyl carbinol urethane), owe their hypnotic effect to different atomic groups. Chloral and its derivatives owe their action to trichlor-ethyl alcohol into which they are decomposed in the blood. The next class represented by amylene hydrate, dormiol and isopral, are secondary and tertiary alcohols, in which an alcohol group is linked with alkyls to a tertiary carbon. The urethanes and hedonal represent the third class, being carbamic acid esters which, because of their very mild action, were soon displaced by a fourth class, the sulphones, sulphonal and trional, which contain four alkyl groups linked to carbon. These possess certain similarities in common with amylene hydrate, since the nucleus of the molecule is a carbon linked to alkyl groups, the resulting hypnotic action being intensified through ethyl groups. These latter compounds serving as models, other nuclei were sought which should contain a tertiary or quaternary carbon linked to the sedative ethyl groups. The ideal groupings which seemed most favorable for these purposes were the substituted urea derivatives, namely, those derived from diethyl-acetyl urea, 1, $(C_2H_5)_2C(H)(CO.NH.CO.NH_2)$ and derivatives of diethyl malonic acid with cyclic structure of the *n* position, as diethyl malonyl urea, 2, $\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!\!>\!C\!<\!\!\begin{array}{l}CO.NH\\CO.NH\end{array}\!\!>\!CO$ and 3, dipropyl malonyl urea. For the production of sleep, the urea group bears an important part, but essential is its linkage with several aliphatic alkyls, rich in carbon, increasing in hypnotic action with molecular weight, reaching a maximum in the dipropyl derivative. Toxic is *N*-methyl malonyl urea, which differs from diethyl malonyl urea (Veronal) in that a methyl group is linked to a

N, like unto the distinction between acetanilid and its methyl compound exalgin. Of these groups, No. 1 possesses a hypnotic action similar to the well-known sulfonal, while No. 3 is about 4 times as active. As a medium between these two, No. 2, Veronal, has merited an unrivaled position among hypnotics. To this class belongs Medinal (Schering), the mono-sodium salt of diethyl barbituric acid, a hypnotic adapted for rectal application.

The search for other fields among the substituted tertiary or quaternary carbon derivatives has led to the old and well-tried valerian; the sedative effect of this on reflex excitability was found to exist largely in the isovaleric acid ester of borneol present in the root. The Riedel Co. introduced this compound under the title of Bornyval; recently a bromin (25%) derivative of this has appeared, namely Brovalol (Valison). To this class belongs the neurasthenic sedative Quietol, claimed to be a propyl valeryl-dimethyl-amino-oxyisobuteryl hydrobromide,

$$CH_3-C(O.CO.C_6H_4)(OH_2N(CH_3))_2.HBr.$$

$$CO_2C_3H_7$$

Related to the phenetidin nucleus is Nevalthein, the sodium salt of *p*-ethoxyphenylaminometa sulfonate. As succedaneum for the alkali bromides, substances free from secondary action peculiar to large doses of these, is Sabromin, a calcium dibrom-behenate (D. R. P. 186,740) analogous to Sagodin, the corresponding iodine compound.

Antipyretics.

The general satisfaction attending the use of phenacetin and other derivatives of the phenetidin nucleus also antipyrin and the various acetanilid combinations has apparently discouraged any further research in this thoroughly explored field. The recent introduction of a Phenetidin Amidoacetate (Voswinkel) presents nothing new over phenocoll (glycocoll phenetidin).

Alkali Iodid Succedaneums

When it is necessary to subject the system for periods, to the action of this halogen and to avoid the undesirable secondary effects, such as usually accompany the profuse administration of iodides, recourse is had to the organic compounds of iodin which are slowly eliminated, exercising thereby a prolonged iodine effect. Most successful among such derivatives are the insoluble alkali earth salts of iodized aliphatic acids of high molecular weight, which liberate their iodine in the organism without the production of the quickly diffusible alkali iodides. Sajodin, the calcium salt of mono-iodobehenic acid, $(C_{22}H_{42}IO_2)_2Ca$ (28% iodine), and Iodthion, a diiodo-hydroxypropanol, $CI_2OH.CH_2CH_3$ (80% iodine), D. R. P. 180,622, 187,822, are representatives of this class. These were followed by Iodival, an α-mono-iodo-isovaleryl urea (47% iodine), $(CH_3)_2CH.CHI.CO.NaN.CO.NH_2$. This, like others of this group, is unaffected by the gastric juice, but in the intestines, it readily dissolves (Knoll Co., D. R. P. 197,648). Iodomenin (an iodobismuth albumin), Iodopeptide (a product of the action of nascent iodine on peptonized albumen, adapted for subcutaneous use), Guaiadol (Fr. Pat. 371,982, a para iodoguaiacol), and Iodomercuric albumin (D. R. P. 177,109) are new.

Synthetic Purgatives.

These are derivatives of either anthraquinone or phenolphthalein. Among the former are Exodin, a mixture of diacetyl rufigallic acid tetra-methyl ether and acetyl rufigallic pentamethyl ether, and Purgatol, a diacetyl anthrapurpurin, bodies built after the emodin (of rhubarb) type, namely, methyl anthraquinone. To the second class belongs the popular non-toxic Purgen or phenolphthalein which is eliminated from the system in practically an unchanged state. New are Aperitol, a valeryl acetyl-phenolphthalein and Sodophthalyl, a disodio quinone phenolphthalein. The esterification of the phenolphthalein serves to render these preparations still more resistive against decomposition in the system. Eulaxans is the sodium salt of phenolphthalein.

Diuretics.

With the discovery of methods for the synthesis of Theophyllin (Theocin) and the introduction of their double alkali acetates and citrates, ideal diuretics seem to have been reached. Of more recent origin are Euphyllin, a combination of theophyllin and ethylene diamine, and Eustenin, the double salt of theobromine sodium and sodium iodide. The latter is employed in arteriosclerosis, aortal aneurism and angina pectoris.

Antirheumatics, Salicylic Acid Derivatives.

The unprecedented success attending the introduction of Aspirin (acetyl salicylic acid) and Mesotan (salicylic methoxy-methyl ester), followed by Spirosal (salicylic monoglycollic ester, U. S. P. 173,776) and Novaspirin (methylene citric acid ester of salicylic acid, Pat. 185,800) has brought out several products built along similar lines. Burroughs, Wellcome & Co. have patented a cinnamyl salicylic acid, Boehringer & Sohn, a salicylo-salicylic ester called Diplosal and Kalle & Co., an acetyl salicylic amide called Arthrisin (D. R. P. 177,054). Diaspirin is a salicylic succinate.

Organic Arsenicals.

Therapeutically valuable arsenicals, especially adapted for subcutaneous use, are obtained through the replacement of the OH groups of arsenic acid by methyl groups, as sodium-methyl arsenate or Arrhenal, $AsO(CH_3)(ONa)_2$, cacodylic acid and its salts. Because of its special value in treatment of the African sleeping sickness (trypanasmiasis), atoxyl has attracted much attention of recent years; this is the monosodium salt of para-amino-phenyl arsenic acid, $H_2N.C_6H_4.AsO(OH)ONa.4H_2O$. In this class of compounds, the arsenic is so finely linked that but very small quantities are taken up in the system. For example, doses of 1 gm. of sodium cacodylate may be taken, although 2/3 of its weight consists of arsenious oxide. Through atoxyl, 40 to 50 times as much arsenic can be administered as in the form of Fowler's solution. Claimed to be an improvement over atoxyl is Acetatoxyl, less toxic and admits ready sterilization. Arsacetin is a sodium para-aceto-amino-phenyl-arsenate, $CH_3CO.NH.C_6H.OH(AsO)ONa$, also proposed as an atoxyl succedaneum. Other arsenicals of minor importance are Thiarsol, a colloidal arsenic-trisulfid; Arsen Triferrol, an arsenic iron preparation of para nucleinic acid; Arsenogen, of like origin; and Sodium Arsenyl tartrate, $NaAsO.C_4H_4O_6.2\frac{1}{2}H_2O$.

Organic Mercurials.

The value of mercurials in syphilitic diseases and also as antiseptics has brought forward a large variety of combinations, some of which, because of ready solubility, freedom from irritation and slow elimination from the system, are

especially adapted for subcutaneous and intramuscular injection; others aim to excel mercuric chloride for local use in being more penetrative (not coagulating albumin) and less irritating. New additions are few. Asquirrol is a stable mercurial, a dimethylate, reacting much like the well-known diphenyl mercury; the greatest care must be exercised in administering this, since through cumulative action, serious symptoms of mercurial poisoning are liable to appear without warning. Asiphyl is mercury paranilide arsenate; Iodargyre and Hydrarsyl are organic mercurials of unknown origin. Mergandol is a mercury sodium glycerate and Antiperiostin a mercuri-iodocantharidate, both being solutions. A colloidal mercurous oxide, prepared by the reduction of mercury salts by the alkali salts of lysalbinic or protalbinic acids or other albuminoids and subsequent dialysis (D. R. P. 185,599–600), has been added to our list of colloidal mercury compounds (U. S. Pat. 740,855). These patents are not unlike those of the Kalle Co. (D. R. P. 179,980), wherein the alkali salts of decomposition-products of albumin are used for preparing colloidal silver and mercury.

Sandalwood Oil Derivatives.

The East Indian sandalwood oil is an old and excellent remedy for gonorrhea, objectionable, however, because of the presence of the terpene, santalen (10%), which causes irritation of the mucous surfaces of the duodenum, the kidneys and also disturbances of the digestion. Semmler[1] found that the chief constituent of this oil was a tricyclic alcohol called α-santalol. Under this title (santalol and gonorol), Mess Heine & Co., of Leipzig, introduced the alcohol into the market. Later, Semmler, through oxidation of this alcohol, obtained the tricyclic aldehyde, $C_{11}H_{16}O$, eksantal and eksantalic acid, $C_{11}H_{16}O_2$. In order to still further avoid any possible irritant action, the OH group of the alcohol was esterified through the salicylic acid radical and the product introduced by the Knoll Co. (D. R. P. 173,240) under the title Santyl. This was followed by the carbonic acid ester Blenyl (v. Heyden, Pat. 182,627). With these as prototypes, the following have been introduced during the past year. Camphosal, the neutral camphoric acid ester of santalol, $C_8H_{14}(CO_2.C_{15}H_{23})_2$, especially adapted for urethral fever and vesical catarrh. Thyresol is a santyl methyl ether of $C_{15}H_{32}OCH_3$, b. p. 149–156° C. (16 mm.). Allosan is the allophanate of santalol. Camphosan, a 15 % solution of camphosal in santalol.

(To be continued.)

NOTES.

A WOOD PRESERVATIVE.

Recently a fence which was built forty years ago on a farm near Mechanicsville, Iowa, was taken down, and the oak posts were found to be remarkably well preserved below ground surface line, where decay of the wood so easily takes place. Four or five inches below the surface there had been inserted in each post at the time the fence was built a wooden plug closing an augur hole cavity that enclosed a reddish, powdery substance. After most of the posts were burned, a section containing the filled cavity was secured. This when split open yielded quite a quantity of the red preservative. The wood surrounding the cavity was perfectly sound, and the augur hole surface was as sharply defined as if made only a few weeks before. The plug was pine, but it had become so hardened that it was whittled with difficulty. The preservative seemed to be only white arsenic, colored by long contact with the wood.

NICHOLAS KNIGHT.

[1] *Ber d chem Ges.*, **40**, 1120.

THE BUREAU OF STANDARDS ANALYZED SAMPLES.

The Bureau of Standards is now able to supply an acid open-hearth steel with 0.4 carbon, in addition to the samples listed in the January number of THIS JOURNAL (p. 41). An acid open-hearth sample with 0.6 carbon will probably be ready by the time this notice appears in print.

Soon after March 1st a change in the fee schedule for the iron and steel samples will go into effect, allowing but a single discount rate as follows:

Single sample of 150 grams, each sample $2.00.

In lots of 3 or more, each sample $1.70.

The sample of zinc ore D of which analysis appeared in the *Jour. Am. Chem. Soc.*, **29**, 269, containing about 31.41 Zn, is in charge of the Bureau and is available for free distribution in approximately 50-gram samples.

W. F. HILLEBRAND.

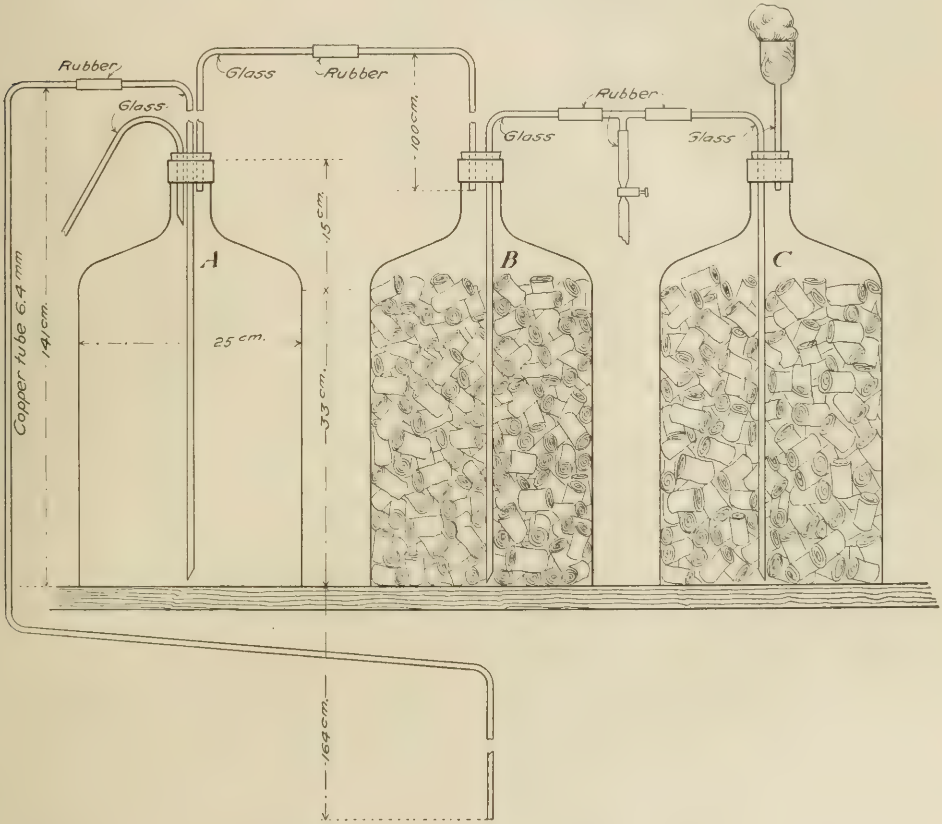
[CONTRIBUTION FROM THE DIVISION OF FOODS, BUREAU OF CHEMISTRY, U. S. DEPT. OF AGR., WASHINGTON, D. C.]

A SIMPLE RAPID PROCESS VINEGAR GENERATOR FOR GENERATOR USE.[1]

In making vinegar on a laboratory scale in which a few gallons only of finished product are required, the existing forms of wooden rapid process generators are unsatisfactory for many reasons. Among these may be mentioned, contamination with the larvae of the vinegar fly, excessive evaporation, and loss by seepage. The essential features of a rapid process generator are, a suitable substratum, usually beech-wood shavings, where the vinegar ferment may develop, a supply of air, and an arrangement whereby the liquor being acetified, is periodically or continuously brought in contact with the shavings. The generator here described consists practically of two glass bottles filled with shavings and suitably connected by glass tubing. The liquor is gradually forced from one bottle to the other and back, using a simple siphon device and a very slow stream of water by which a third bottle is alternately filled and emptied. Contamination from the outside is entirely avoided by filtering all air admitted through a cotton plug. There is probably little evaporation as excessive heating does not occur, and there is no loss possible by seepage. Three five-gallon bottles, *A*, *B*, and *C*, are connected as shown. The heights indicated of the various tubes are essential to the proper operation of the apparatus and cannot be materially lessened. The use of a siphon to secure the periodic wetting of the shavings was suggested by Dr. C. S. Hudson. Its down-coming arm is made of copper tubing to lessen the danger of breaking. The bend shown in this arm appears to be necessary in order that the siphon shall not start promptly when the water overflows. A slow drip of water is run in through the curved tube in the stopper of bottle *A* at such a rate that several hours are required for *A* to fill. The volume of *A* is larger than that of *B* or *C* by the volume of shavings in

[1] Published by permission of the Secretary of Agriculture.

B or *C*, and as *A* fills, not only is practically all of the liquor forced from *B* to *C*, but considerable quantities of air pass up through *C* and out. As *A* empties, the liquor passes back from *C* to *B*, and considerable air is drawn from *C* through *B* into *A*. In this way the air of the generator is continually being partly replaced by fresh air. When once started, the generator requires no further attention,



and acetification is usually complete in a few weeks, working at room temperature. The shavings have a clarifying effect on the liquor so that when the finished vinegar is withdrawn it is brilliant. The generator is filled and emptied through the T tube between bottles *B* and *C*. When not in use these bottles should be kept full of vinegar. It is evident that the device can be operated on a smaller or larger scale than the one shown. The present size will produce about three gallons of vinegar at one charge.

H. C. GORE.

NOTE ON TURPENTINE.

Replying to Mr. R. H. Acott's statement in the February number of THIS JOURNAL, as well as to several inquiries from other readers, the writer wishes to state that in his article, in the January number, on "Turpentine and Its Adulterants," the terms "very light naphtha" and "exceedingly light petroleum products" were *NOT* intended to include ordinary gasoline, but merely such *unusual* products as "hexane" petroleum ether, etc.

Inasmuch as the writer's statement that his method gives low results with such products, if understood according to Mr. Acott's interpretation, and coupled with his statement as to the use of gasoline for adulteration, would greatly reduce the general applicability and utility of the method, the writer desires to say that he too, has frequently found samples of turpentine adulterated with petroleum products resembling gasoline, and that the method described, gives excellent results (90 per cent. on known mixtures) in such cases.

The writer has also received a number of inquiries concerning the conditions of observation of the butyro-refractometer readings.

The reasons for employing these readings rather than any other physical constant, were ease of application and smallness of amount required, the time consumed being but a few moments, and a drop or two of material being amply sufficient for the determination.

The readings given in connection with the fractionation results are supplied merely to show the impracticability of arriving at quantitative results by that method. Some other physical constant might have been used, and undoubtedly have answered equally as well.

The readings given in connection with the writer's method —and I would emphasize that these *are by no means an essential part of the method*—are interesting merely as they demonstrate the possibility of recognizing, very quickly, approximately, the *kind* of petroleum products used, low readings indicating light products, high readings, heavier ones.

The writer took the readings at 25° C., and used ordinary white light, those being the most convenient conditions; and these having been used throughout, the figures given, are comparable with each other. It is assumed that each operator, before using this or any other similar new method, will try it on known substances, and will use his own standards and constants, as a basis for comparisons and conclusions.

ARTHUR E. PAUL.
LABORATORY OF MARINER AND HOSKINS,
CHICAGO, ILL., Feb. 13, 1909.

DETERMINATION OF ACETANILID IN HYDROGEN PEROXIDE SOLUTIONS.

Recently I had occasion to determine the proportion of acetanilid in a commercial sample of hydrogen peroxide. Our client stated that one chemist whom he had consulted on the subject, declared it to be impossible, and it must be admitted, that so far as the literature is concerned, there seems to be nothing to fit that particular case.

It is a matter of record that boiling acetanilid with strong hydrochloric acid or with strong caustic alkali, causes a dissociation, with formation of anilin. The reaction is quantitative. The method of Seidell[1] depends on this conversion by acid. A five minute vigorous boiling in a solution containing about one-fourth of concentrated hydrochloric acid was found by him sufficient to effect the change. That observation I have been able to confirm. In the solution after cooling it was found possible to determine the anilin by titration with Koppeschaar's solution—practically the solution used in urea determinations diluted to a convenient strength. The end reaction is when all of the anilin has been precipitated as the bromine substitution product, when the excess of bromine imparts a yellow tinge to the solution. For standardizing or for determining acetanilid in many pharmaceutical preparations, his process serves very well, but in the presence of the peroxide, the preliminary boiling completely destroys the acetanilid, affording a yellowish solution in which bromine gives no precipitate.

It was found that the desired result could be obtained by boiling with strong caustic alkali in presence of granulated zinc, and distilling over the anilin formed, by the aid of a current of steam. After some experimenting, the following plan was worked out: In a side-neck flask of 200 cc. capacity, place about half a stick of caustic potash or soda (6–7 grams). Add about 20 cc. of water to dissolve, and then 25–30 grams of granulated metallic zinc (the zinc had best be in as fine particles as can be obtained in "granulated" form. There is reason, however, to believe that "zinc dust" is too finely divided for this purpose). Then add a measured amount (not over 50 cc.) of the solution to be tested. Connect the flask on the one side with a flask to supply steam, arranging the tube to deliver steam near the bottom of the solution; connect on the other side with a condenser. The condenser should deliver into a Peligot bulb tube or some other arrangement by which the distillate is immediately brought in contact with moderately strong hydrochloric acid.

Raise the heat on the flask slowly, and when nearly half of the contents have distilled over, start the steam to passing through. The end of the distillation is a matter of guess. When the anilin is coming over in quantity, fumes are to be seen in the receiver, but for the last portions they cannot be seen. When it is judged that all has come over, detach the receiver and catch what comes over later in a fresh receiver or a beaker, and titrate it separately.

To prepare the volumetric bromine solution, dissolve 25 grams of caustic potash in 20–40 cc. of water, cool, and add liquid bromine until it appears supersaturated. Then dilute to about 200 cc. and boil out excess of bromine (judged by the color). Cool, and dilute to one liter. This should give a solution of which 1 cc. = nearly 0.01 gram acetanilid. Standardize by means of a solution containing 0.5 gram acetanilid in 200 cc. of water, using 30–50 cc. lots at a time, treated either by distillation on the manner above given, or by boiling with strong hydrochloric acid. Either method was found to give the same result with the same amount of acetanilid.

The method was tested by first distilling known quantities of the sample and titrating the distillate, then adding known amounts of acetanilid to the same quantities of the sample, and distilling. The distillates took just the additional amount required by the acetanilid added.

The presence of acetanilid was indicated by obtaining the iso-nitril reaction on the original sample.

ELWYN WALLER.

[1] J. Am. Chem. Soc., 29, 1091.

NOTE ON MR. BAILEY'S PAPER ON ACCURACY IN SAMPLING COAL.[1]

In the carefully planned and admirably carried out series of experiments described in his paper Mr. Bailey has shown that the errors due to sampling are likely to be much larger than most of us have realized. While the paper deals specifically with coal, the conclusions are applicable to the sampling of all mixtures of solids. It is the first attempt that has been made to measure quantitatively the errors due to too small an initial sample and to insufficient crushing before quartering. No one realizes more fully than Mr. Bailey that there are other parts of sampling than those he has investigated, in which serious errors may occur. The U. S. Steel Corporation have studied some of these and formulated rules for taking samples of their principal raw materials.

This society and others have done much to insure the introduction of more accurate methods of analysis, but no one has done anything to insure that the samples represented the material correctly. To insist on the use of methods that

[1] THIS JOURNAL, March, 1909.

are accurate to a few hundredths of a per cent. and accept samples that have an error of several per cent. is absurd; but it is what most of us have done.

Many of the complaints that are made of inaccurate analyses are due to inaccurate sampling. We have "strained at a gnat and swallowed a camel." Now that attention has been drawn to this matter it is to be hoped that the American Chemical Society will take it up energetically, study the question thoroughly and formulate rules for sampling, and, as far as possible, insist that its members follow these rules, or, at least, that all certificates of analysis state how the samples were taken.

George C. Stone.

DISCUSSION ON "ACCURACY OF SAMPLING COAL" BY E. G. BAILEY.[1]

Mr. Bailey's paper is so interesting, instructive and comprehensive that it will require a great deal of study, before one can discuss it intelligently.

Mathematics that have lain dormant for years must be reviewed and some parts carefully studied before the full value of Mr. Bailey's paper can be realized and appreciated.

The application of the mathematical principle of least squares, a principle based on the theory of probabilities and the general law of deviations, to the sampling of materials, in order to test the accuracy of different methods, is unique and is worthy of much praise.

The maximum errors are here shown, and probable and possible errors are calculated to a mathematical certainty, thereby throwing additional light on a very important subject that needs illumination.

The proper sampling of non-uniform material under the varying conditions in which it must be sampled, is so difficult that in many cases it seems almost impossible to obtain a representative sample. Duplicate sampling by the same method or by different methods at times give very consistent results; at other times, results obtained indicate that no method of sampling, so far devised, will properly represent the material.

By applying the principle of least squares to the different methods, that method that gives least variation (if applicable to the varying condition of sampling), may be selected and in so doing material progress may be made.

Reference is made to publication of U. S. Geol. Survey, in which heavier pieces—such as slate and pyrites—settle to the bottom of the car in transit. Experiments made on Illinois and Indiana coals transported about 150 miles, prove that a settling of heavier particles does occur. Results in the main corroborate those of the U. S. Geol. Survey. For this reason sampling from the surface of cars has been discontinued.

The importance of total weight of sample, the relation of size, weight of pieces taken to the total weight of sample, and the limit beyond which sample should be divided when crushed, is especially instructive. A statement showing relative weight of sample taken to total weight of material sampled, would be very interesting.

The amount of experimental data given, shows the thoroughness of Mr. Bailey's work, and the paper as a whole is a valuable addition to the literature of sampling materials.

W. Brady.

[1] See March Number, This Journal.

SOIL FERTILITY.

The following correspondence on the subject of soil fertility is self-explanatory. The first letter, dated January 21st, was sent to a number of agricultural experts by Dr. A. M. Peter, chief chemist and head of the Chemistry Division, Kentucky Agricultural Experiment Station, at Lexington. The second letter is a letter of transmittal by Dr. Frank K. Cameron, Bureau of Soils, Department of Agriculture, and joint author of Bulletin No. 22 of that Bureau. The third letter dated January 28th, is Dr. Cameron's letter expressing his position and views. The fourth letter, dated February 18th, summarizes the replies up to that time by Dr. Peter, in answer to his first letter of January 21st.

Kentucky Agricultural Experiment Station,
State University.
M. A. Scovell, *Director*. *Chemical Division.*
A. M. Peter, *Chief Chemist, Head of Division.*
S. D. Averitt, *Chemist.*
O. M. Shedd, *Chemist.*

January 21, 1908.

Dear Sir:

In a "Hearing before the Committee on Agriculture of the House of Representatives," 1908, Drs. Whitney and Cameron, of the Bureau of Soils, have made statements to the effect that the recent teachings of the Bureau in regard to soil fertility are generally accepted throughout this country and Europe and that they are being widely taught in the Agricultural Colleges of this country. The teachings referred to, with which you are, no doubt, familiar, may be summarized in the following statements:

(1) That all soils contain enough mineral plant food in available form for maximum crops and that this supply will be indefinitely maintained.

(2) That the real cause of infertility is the accumulation in the soil of poisonous excreta from plant roots.

(3) That it is not ever necessary to add fertilizers for the purpose of increasing the plant food in the soil, the good effect of fertilizers being due to their power of neutralizing or destroying these toxic substances or their activity.

(4) That soil fertility can be maintained indefinitely by practicing a system of rotation by which a crop is grown each year that is not injured by the excreta of the preceding crop.

In order to ascertain just how extensively these views are accepted and taught in our Agricultural Colleges and Experiment Stations, the writer is sending this letter to professors of agriculture, agronomists and agricultural chemists in all such institutions on the "Organization Lists." It is proposed to publish a summary of the data obtained, without giving names of institutions or individuals. Will you kindly assist by telling me whether or not these views are accepted and taught by you or your institution, or by referring this letter to some one who will give me an authoritative answer? Yours very truly, Alfred M. Peter.

United States Department of Agriculture,
Bureau of Soils, Washington, D. C.

February 5, 1909.

Dear Sir:

I have been advised by Dr. A. M. Peter that recently a

circular letter had been sent out by him, in which are summarized certain views regarding soils, and these views are attributed to me. I deem it proper that a copy of my reply to Dr. Peter should be in the hands of every one reached by his letter. I may say that in a letter dated February 3rd, Dr. Peter concurs in this opinion. I am therefore enclosing for your consideration a copy of this reply.

Very truly yours,

FRANK K. CAMERON, in charge.

Dr. A. M. Peter,
Ky. Agr. Expt. Station,
Lexington, Ky.

UNITED STATES DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS,
WASHINGTON, D. C.

Physical and Chemical Investigations.

January 28, 1909.

Dr. Alfred M. Peter,
Ky. Agr. Expt. Station,
Lexington, Ky.

MY DEAR DOCTOR PETER:

I have received your letter of the 22nd, enclosing a circular letter, and I have also seen your letter to Professor Whitney. I recognize, of course, that you disbelieve my statements or seriously doubt them, and ordinarily I should be disposed to give the matter no further consideration than an acknowledgment of your courtesy in advising me of your intentions. My high respect for you personally and our past pleasant relations have induced me, however, to treat the matter differently. Assuming that you desire to undertake your investigations in a disinterested spirit, I wish to submit some criticisms to your consideration. You summarize my teachings under four heads, which I will consider seriatim:

"1. That all soils contain enough mineral plant food in available form for maximum crops and that this supply will be indefinitely maintained."

I do not teach this doctrine, nor have I ever taught it. From Bulletin No. 22, Bureau of Soils, of which I was a joint author, I quote those passages which seem to me to bear upon this point:

Page 49. "It will be seen from the results obtained by this Bureau that these large annual applications of stable manure, or of high-grade fertilizers, do not apparently change permanently the chemical composition of the soil as determined by chemical analysis of the aqueous extracts; that is to say, immediately after the application the influence of the fertilizer can be seen in the increase in the soluble salt content of the soil; but not only is this comparatively slight, but fields that have been annually treated in this way for a number of years do not show on the average appreciably more water-soluble plant food than adjoining soils upon which no such applications have ever been made.

"These observations indicate obviously that fertilizers do sometimes increase the yield of crops and maintain a larger average yield over a period of years. But it is not obvious, as has been claimed, that such results indicate in the unfertilized soil an amount of available plant food actually insufficient for the need of crops."

Page 50. "If fertilizers have any influence upon the texture of the soil, or upon the movement of soil moisture, they will not only influence the supply of water which will be delivered to the plant, but also the supply of nutrient materials normally contained in this water. The problem would then come into the domain of soil physics rather than into that of soil chemistry. The important practical inference, if this is so, is that fertilizers have to a certain extent the same effect as cultivation and cropping; but in a majority of cases it is undoubtedly better to depend upon efficient methods of cultivation and cropping than to rely upon fertilizers while at the same time neglecting to give proper attention to the physical condition of the soil. The effect due to cultivation is also more permanent than the effect due to fertilizers. Furthermore, the influence of fertilizers on the yield of crops is not proportional to the amount of fertilizer added, as it frequently happens that a small application is quite as efficient as a larger application."

Page 53. "The texture of the soil is the principal basis for the classification of soils in the soil survey, and taken in connection with the character of vegetation and the experience of farmers is undoubtedly a safe and reliable one for the estimation of the relative value of soils for certain crops and for determining the most efficient methods of cultivation. It is realized that the controlling effect of the physical properties of soils on crop distribution and production does not depend wholly upon the texture of the soil, as shown by the mechanical analysis, but that there are two other very important properties, the organic matter content and the structure of the soil, or the arrangement of the soil grains. Unfortunately no satisfactory methods have been devised to determine this structure or its consequent effects. Not only is the character and yield of a crop adapted to a soil dependent upon the texture and structure, but upon the moisture which the soil can deliver to the plant to supply its needs."

Page 55. "It is becoming increasingly evident that this capacity of a soil to deliver water is a very important and probably the most important factor in crop production, and this is a point which will receive consideration in the future work of the Bureau. The delivery of water from the soil to the plant must receive more consideration in future chemical studies of soil for the reason that it is the mechanism by which the mineral nutrients are supplied to the plant, and it is evident that if the delivery be small, the plant will suffer not only for water itself but also for the mineral food which the water supplies, even though ample quantities may be present in the soil solution, and in what would usually be regarded as readily available form. This point of view aids in understanding many of the discrepancies between chemical indications and actual crop returns in past work, and conclusively shows that a chemical study of a soil, which does not include as well a physical study along the lines here suggested, can not be expected to yield definite results."

Page 58. "There is no question that in certain cases, and in many cases, the application of commercial fertilizers is beneficial to the crop. The experience of farmers, the enormous sums expended for commercial fertilizers, and the many experiments carried on at the experiment stations prove that under certain conditions fertilizers are very beneficial in increasing the yield of crops. The fundamental idea under all of this work, however, has been that of supplying plant food in an available form; that is, adding

to the supply existing in the soil. It is significant that other conditions of growth have so much influence on the yield that in but very few instances, even after long-continued experiment, has it been demonstrated that any particular fertilizing ingredient or ingredients are required for any particular soil, and that even then the effect of the fertilizer varies so greatly from year to year that no specific law has been worked out, even for a particular soil, from which the fertilizing requirements could be deduced in any exact manner.

"It is also significant that, in general farming, fertilizers are most useful in the early stages of the growth of plants, and the common practice is either to put the fertilizer in with the plant or to put it in at some time before the seed is planted. Very little effect is obtained in field culture in attempts to increase the value of a crop showing signs of inferior growth, by the application of fertilizers. This would indicate that the effect is early and immediate. In opposition to this may be cited the special cases of the application of nitrates to increase leaf development, potash salts to increase starch, and many similar cases, particularly in greenhouse culture, to hasten the maturity, to prolong the growth, or to produce artificial stimulation of certain plant processes. But the use of fertilizers in such cases is recognized as producing artificial and abnormal conditions."

Page 60. "One possible explanation of the effect of fertilizers, which would be in entire accord with the hypothesis that has been formulated, is that the fertilizer is needed during the early period of growth when the root system is beginning to develop, that is, as the plant germinates and begins to feed upon the soil the root system has to be artificially nourished by a temporary increase in concentration as regards one or more constituents, whereas, when the root system is developed into a considerable volume of soil the plant will be quite capable of collecting all of these materials it may require. It is a fact, admitting of no argument, that fertilizers rarely take the place of efficient methods of cultivation and of cropping in increasing or maintaining crop yields."

Page 6. "We have examined a few cases, such as certain samples of the Galveston sand, which showed practically none of the several necessary mineral plant foods to be present and soluble, but neither will these samples in their natural state support any crop, being nearly pure silica, and as such can scarcely be regarded as soils. Practically, all soils were found to give a solution with a composition varying little from a normal, but even the exceptional soils showing extremely small quantities of one or more soluble plant food constituents would still yield a fair crop if brought into good mechanical condition.

"The idea now held by the Bureau as a result of these investigations is that the ratio of the nutrient elements in normal soils does not play a very important part in the yield of crops, or, to be more explicit, low yields are usually related to the physical condition and characteristics of the soil, and that it is only after these major controlling factors are changed and the yields thereby increased, that it would be necessary or profitable to consider this question of the ratio of plant foods. In other words, that it is only where all other conditions of plant nutrition and growth are satisfactorily controlled that the nutritive ratio can be considered an important factor and that the influence of this would be mainly seen in the quality of the crop rather than in the yield."

Pages 63 and 64. "The exhaustive investigation of many types of soil by very accurate methods of analysis, under many conditions of cultivation and of cropping, in areas yielding large crops and in adjoining areas yielding small crops, has shown that there is no obvious relation between the amount of the several nutritive elements in the soil and the yield of crops; that is to say, that no essential chemical difference has been found between the solution produced in a soil yielding a large crop of wheat and that in a soil of the same character in adjoining fields giving much smaller yields. The conclusion logically follows that on the average farm the great controlling factor in the yield of crops is not the amount of plant food in the soil, but is a physical factor, the exact nature of which is yet to be determined.

"It is not to be deduced from this that fertilizers do not frequently increase the yield of crops, but whether this increase is due to an actual increase of the plant food in the soil, to an early stimulation of the plant to enable it to get its roots out into a sufficient volume of soil, or to some physiological or physical effect is not altogether clear. As above stated, the effect of fertilizers on the quality of the crop is not specifically considered in this bulletin.

"The results of these investigations also seem to indicate that the actual quantity of water a soil can furnish the plant, irrespective of the percentage of water actually present in the soil, has probably a very important influence on the yield. When the supply of water is inadequate to the need of the plant, as the water is a medium for the conveyance of nutritive solutions to the plant, it may well indicate not only a deficiency in the supply of moisture, but also of nutrient material contained in the water. It may be, moreover, that with an insufficient water supply, and consequently an insufficient food supply, fertilizers, by temporarily increasing the concentration of the solution, may increase the food supply of the plant; but as in this case also the obstructive factor is the purely mechanical function of delivering water from the soil to the plant, the problem is one to be handled by physical methods, and can not, in the nature of the case, be solved by chemical methods alone.

"Again, while some variations occur in the composition and concentration of the soil solution, in the case of the great majority of cultivable soils these variations are within comparatively narrow limits. The nature of the solution is but seldom permanently affected by the addition of ordinary mineral fertilizers, and it seems safe to say, therefore, that the concentration with respect to the mineral plant food constituents per unit of solution is approximately constant. Considering the wide variations in the percentages of water present in different soils, however, the amounts of dissolved plant foods in them may be quite different.

"The conclusion seems justified that, although differences in the dissolved salt content, or in the concentration and composition of the soil moisture, may be a factor in the yield as well as quality of a crop, it does not appear to be a major one in determining or controlling the wide variations observed in crop yields on different soils. It appears further that practically all soils contain sufficient plant food for good crop yield, that this supply will be indefinitely main-

tained, and that this actual yield of plants adapted to the soil depends mainly, under favorable climatic conditions, upon the cultural methods and suitable crop rotation, a conclusion strictly in accord with the experience of good farm practice in all countries."

Neither from these passages, nor any others in the bulletin, nor any others that I have ever written so far as I can recall can the conclusion be fairly drawn that I teach that *maximum* crops can be grown without the use of fertilizers. I have never taught that in the case of any given soil and crop a larger yield could not be obtained if larger amounts of soluble mineral nutrients were present. I have taught that cases may exist where there is not sufficient "available" plant food in the soil (see specifically citation above, p. 62, Bulletin No. 22); and also that cases may exist where the rate of supply of moisture containing mineral plant food from soil to plant is insufficient, as cited above. These cases, however, are to be considered as abnormal. I have taught, however, that the "plant food" explanation of fertilizers is insufficient in itself to account for the known facts. That (speaking generally and with consideration of exceptional cases) the soil solution in all soils tends towards a normal concentration which is the same for all soils, as regards the constituents derived from the soil minerals, and this concentration is, normally, sufficient to give good (not the maximum possible) crop yields. These conclusions follow from *a priori* considerations and experimental evidence advanced in Bulletins Nos. 22, 30, and 50.

To sum the matter up, I believe and teach that mineral fertilizers are useful as one of the three general methods of soil control, but that they have other and probably more important functions than supplying plant food.

I wish to say here, that on re-reading carefully Bulletin No. 22, I feel that there are but two material points on which just criticism may be made: The tables are badly arranged and do not bring out in themselves that the same fields were examined at intervals. And, secondly, the nitrate determinations are probably valueless, for subsequent investigations have shown the analytical method to be doubtful; nitrates are now known to vary very widely within a few hours, and more especially because nitrates are not derived from the soil minerals, and should not be regarded as mineral components of the soil solution.

"2. That the real cause of infertility is the accumulation in the soil of poisonous excreta from plant roots."

To represent correctly my views and teachings, this statement would have to be materially changed. So far as I can recall I have never ascribed infertility to any one cause. Definite organic compounds injurious to certain plants have been extracted from the soils. Experimental evidence has been obtained which indicates strongly, if not positively proving, that such substances are excreted by plant roots. To correctly represent what I have taught your statement should be amended to read: One of the causes of infertility is the accumulation in the soil of injurious organic matter, possibly excreted from plant roots.

"3. That it is not ever necessary to add fertilizers for the purpose of increasing the plant food in the soil, the good effects of fertilizers being due to their power of neutralizing or destroying these toxic substances or their activity."

This statement does not represent my views or teachings. It should be amended and restated as two separate and distinct propositions. First, the increase in mineral plant nutrients due to an ordinary fertilizer treatment is insufficient to explain the improved plant growth. Second, one of the possible functions of a fertilizer treatment of the soil is to affect the organic matter in the soil in a way advantageous to plant growth.

It has been conclusively shown that the presence of mineral salts affects the rate of oxidation of organic matter by root growth. Other effects on the organic substances of the soil have been strongly indicated if not conclusively proven.

"4. That soil fertility can be maintained indefinitely by practicing a system of rotation by which a crop is grown each year that is not injured by the excreta of the preceding crop."

While I do not recall teaching the doctrine as stated above I think that a soil may be maintained permanently in a more or less good condition for plant growth without the use of fertilizers, by adopting a suitable crop rotation. But I have always taught that it was better and more economical to use fertilizers as an additional method of controlling the soil and soil conditions.

I have, of course, taught that one of the purposes of using a crop rotation was to overcome the harmful influences of the preceding crops, among which influences is the organic débris from the preceding plant life. Some of this débris, in some cases very probably, is material excreted by roots during growth. That rotations are practiced for other purposes, such as for instance the elimination of parasitic growths, injurious insects, etc., is accepted by every one so far as I know, and certainly has been an integral part of my teachings, although I have never made any special investigations in this direction and consequently have had no occasion to dwell upon it in my writings.

I am not aware that the views you attribute to me are being taught anywhere. Certainly I would never teach them myself. But the views which I do hold are being taught in whole or in part at a large number of our American institutions, and some of my more important publications have been translated into foreign languages. I see no reason to alter or modify the testimony I gave to the House Committee on Agriculture.

Finally, I submit that it is unfortunate that you take the attitude expressed in your letter towards the physical chemists, etc., for it has been the applications of the principles and methods of physical chemistry and physiology that have made my work possible. It would seem obvious that the commendation of specialists in these lines would have at least as much weight as the opinions of agriculturists and agronomists who have not had any training or experience in these methods of modern chemistry.

I feel that in view of the action you have taken, a copy of this letter should be placed in the hands of each and every one to whom your circular letter was addressed. I must therefore request that you furnish me at your earliest convenience such a list as will enable me to do this. For your convenience I am enclosing an extra copy of the "organization lists" and a franked envelope.

Very truly yours,

FRANK K. CAMERON, in charge.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,
STATE UNIVERSITY.

M. A. Scovell, *Director*. *Chemical Division*.
A. M. Peter, *Chief Chemist, Head of Division.*
S. D. Averitt, *Chemist.*
O. M. Shedd, *Chemist.*

LEXINGTON, KY., February 18, 1909.

DEAR SIR:

Replies to my letter of January 21st have now been received from 104 individuals in the United States and Canada, including 35 Agricultural Chemists, 25 Agronomists, 21 Professors of Agriculture, 9 Soil Specialists, both chemists and physicists, 8 Experiment Station Directors, not otherwise classified, 3 Directors of Farmers Institutes, 1 Professor of Vegetable Pathology, 1 of Horticulture and 1 of Natural Science. Out of these only two endorse the Bureau's views without qualification and say they are taught in their institutions as established facts. These two are from minor or branch institutions, however, not one of the Land-Grant Colleges or State Experiment Stations being willing to accept or teach them in the sense in which they have been put forward by the Bureau. About half recognize more or less truth in the doctrines and present and discuss them in advanced teaching. Most of these recognize the value of the Bureau's work on toxic substances and consider them a possible factor in soil fertility, though not the most important one. The rest either say they do not accept and teach the Bureau's views on these subjects, or oppose them. The Agricultural Colleges and Experiment Stations in 47 states and territories of the United States are represented in these answers, showing a very general interest in the subject of the inquiry. It is apparent that, while the Bureau's views on soil fertility are not being accepted and taught as established, in these institutions, they are being generally presented and discussed in advanced teaching of agriculture.

In a letter to me dated January 28th, a copy of which has been sent to you, Dr. Cameron takes exception to my presentation of the Bureau's teachings and explains his position in this matter. Dr. Whitney in a letter to me approves Dr. Cameron's letter, so it may be taken as an authoritative expression of the Bureau's views. If, after reading it, you desire to modify your opinion already expressed to me, I will be glad to hear from you before making my final publication.

Yours very truly,
ALFRED M. PETER.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The following letter and minutes on this subject are self-explanatory.

NEW YORK, February 10, 1909.

DEAR SIR:

The International Congress of Applied Chemistry will meet in London in the week of May 27 to June 2, 1909. In the past Paris, Berlin, Vienna and Rome have enjoyed the honor of entertaining this most distinguished body of scientists. It is now proposed to issue an invitation to the London Congress to hold its next meeting (Spring, 1912) in New York City.

As the U. S. Government does not coöperate in such meetings nor does it help to defray expenses, it is left to the American chemists, and especially to those connected with chemical industries, to take the initiative and responsibility.

A temporary committee has therefore been formed to consider, first, whether it will be practicable and wise to issue such invitation; and second, if decided in the affirmative, what steps shall be taken to issue it and make it effective; and it has been decided to request all those who might be interested and who might assist in the matter to attend a meeting to be held on Saturday, February 20th, at 8.15 P.M., at the Chemists' Club. You are earnestly requested to be present.

THE TEMPORARY COMMITTEE.

Wm. H. Nichols, *Chairman*; Albert Plaut, *Treasurer*; H. Schweitzer, *Secretary*; Charles Baskerville, *First Vice-Chairman*; Marston T. Bogert, *Second Vice-Chairman*; L. H Baekeland, Charles F. Chandler, John Hays Hammond, J. Hasslacher, Alex. C. Humphreys, W. R. Ingalls, Adolf Kuttroff, Morris Loeb, W. J. Matheson, H. A. Metz, William McMurtrie, T. J. Parker, Cl. Richardson, Wm. J. Schieffelin, I. F. Stone, Maximilian Toch.

Minutes of meeting, called by the Temporary Committee to discuss advisability of holding the Eighth International Congress of Applied Chemistry in New York City and held in the Chemists' Club on February 20, 1909.

Present, W. H. Nichols, Chas. Doremus, Walker Bowman, Chas. Baskerville, Wm. H. Erhart, J. Hasslacher, M. T. Bogert, L. Baekeland, J. W. Richards, E. Schill, E. G. Love, T. J. Parker, I. F. Stone, L. Briggs, E. F. Roeber, W. J. Evans, H. Schweitzer, Wm. H. Nichols in the chair.

After a few introductory remarks by the chairman, H. Schweitzer read the minutes of the first meeting and many letters which were received favoring the plan of inviting the Eighth Congress of Applied Chemistry to New York.

The question, whether it is practical and wise to issue such an invitation was first discussed and finally a motion brought by Mr. Bogert, seconded by Mr. Parker, that it is the sense of this meeting that such steps should be taken as appear necessary or desirable to extend an invitation to hold the Eighth Congress of Applied Chemistry in New York, was unanimously carried.

It was then discussed what steps should be taken to make the invitation effective, and upon a motion by Mr. Hasslacher, seconded by Mr. Doremus, it was decided to authorize the secretary to correspond with such scientific organizations, educational institutions, manufacturing corporations, etc., likely to be interested in the Congress, to designate official delegates and alternates to meet at the Chemists' Club on Saturday, April 3rd, at 8.15 P.M. If distances should forbid the attendance of delegates, communications on the part of the addressed should be solicited.

As it was considered essential to issue the formal invitation to the London Congress through the U. S. Government, a committee was selected to take appropriate steps to accomplish this object.

The committee consists of Wm. H. Nichols, Chas. F. Chandler, Ira Remsen, J. Hasslacher, W. R. Whitney, A. Plaut, L. Baekeland, M. T. Bogert, D. T. Day, J. A. Holmes, C. D. Walcott, H. W. Wiley, Chas. Doremus, H. Schweitzer, and Chas. Baskerville, *chairman.*

The committee was given power to add to its number.

The secretary was requested to notify the English Con-

gress officials about the progress made by this committee.

Adjourned to April 3rd at 8.15 at the Chemists' Club.

H. SCHWEITZER, *Secretary.*

COMMITTEE ON ANALYSIS OF FATS, SOAPS AND GLYCERINE.

The following letter has been issued by the Special Committee on Glycerine:

American Chemical Society Committee on Uniform Tests of Glycerine: A. C. Langmuir, *Chairman*, B. T. B. Hyde, R. E. Divine. Office of the Chairman: 9 Van Brunt Street, Brooklyn, N. Y., U. S. A.

GENTLEMEN:

The Committee on Uniformity of Technical Analysis of the American Chemical Society has appointed a sub-committee to study the merits of the various methods in use for the sampling, analysis, and valuation of crude and dynamite glycerine.

At present there are often radical differences between analyses of the same glycerine by different chemists. The chief reason is undoubtedly due to the use of a number of methods and individual modifications of these methods.

It is the purpose of this committee to correspond with buyers and sellers of glycerine, manufacturers and chemists, to compare the methods in use, note their defects, if any, and point out improvements, if possible. Finally a method will be recommended which is believed to be the best for the purpose of obtaining correctness of results, giving due consideration to present general practice.

With this end in view we invite the coöperation of manufacturers, works chemists and commercial analysts. It is only by free discussion and criticism that the end can be obtained.

As a beginning the committee outlines below some points brought out by their own experience and indicates some of the problems to be solved, as follows:

ANALYSIS OF CRUDE GLYCERINE AND WASTE SOAP LYES.

One of us favors in his own work the Hehner method as modified by Richardson and Jaffe. Another uses the Hehner method, and the third has used chiefly the acetine method.

Acetine Method.—This method has been criticized as giving results below the truth. Geitel (*J. prakt. Chem.* (N. F.), 55.429) found only 97–8 per cent. on testing anhydrous glycerine, sp. gr. 1.2654. Filsinger (*Ztschr. angew. Chem.*, 1889.3) found on C. P. glycerine 86 per cent. only 83.7 to 84.2 per cent. One of us has verified the above.

On the other hand, Lewkowitsch prefers the acetine to the bichromate method. It is no doubt far superior to the bichromate in the analysis of foods and very low-grade glycerines.

The acetic anhydride is variable and should be tested. The end-point in the titration is sometimes troublesome to decide.

Bichromate Method.—The oxidation of glycerine to carbon dioxide by acidified bichromate is probably incomplete. Traces of formic acid or formaldehyde and carbon monoxide may be formed. One of us has identified the latter in the gas evolved. If the error due to the above is to be constant, conditions as to temperature, concentration and time should be definitely stated. Under the conditions of the Richardson and Jaffe method[1] one of us obtained 99.4 to 99.6 per cent. glycerine on C. P. anhydrous glycerine.

This loss is probably offset by oxidizable impurities not removable by silver oxide or basic lead acetate such as glycol, polyglycerols and certain albuminoids. The lower fatty acids, contrary to the general belief, have some reducing action on bichromate.

Silver oxide is omitted in the Richardson and Jaffe method as superfluous, lead acetate alone being used. As this does not remove all chlorine, it is well to add to the filtrate a little silver acetate. It is better to remove any excess lead before oxidation.

If silver oxide is used slightly higher results are obtained.

The use of a stock solution of bichromate is open to objections. It is better to weigh than to measure. One of us prefers to weigh out the dry bichromate for each test.

The bichromate is probably the most reliable basis. It is better to take it as pure rather than to standardize against iron. In reference to its equivalent weight with respect to glycerine the one in general use, *i. e.*, 7.486 = 1 gram glycerine is not in harmony with recent atomic weight tables.

If Mohr's salt (ferrous ammonium sulphate) is used in the regular analysis it should not be assumed to be pure, as it is variable in strength and should be tested against bichromate.

The analysis should be carried through promptly. An aqueous solution of glycerine may ferment. The oxidation mixture will change in bichromate strength unless dust is excluded. All apparatus must be scrupulously clean and should be used for no other work. It is well to run a blank occasionally with the reagents and distilled water.

The degree of basicity of the lead acetate has been said to exert an influence on the results, an excessively basic acetate throwing down some glycerine as glycerate. This has been noted by some of us when using a large excess of acetate in the analysis of spent lyes.

In the valuation of crude glycerine, a knowledge of the amount of impurities in addition to the per cent. of glycerine is very desirable as these increase the difficulty of refining. A definition of the term "organic impurities" is advisable. The committee has not yet found any reliable method, particularly on soap lye crudes.

DYNAMITE GLYCERINE.

With respect to testing dynamite glycerine the problems are simpler.

Salt is generally determined by titration after burning off glycerine or by testing the diluted sample. The latter is more convenient and seems to give equally accurate results.

Specific gravity is found by the pycnometer, Westphal balance, or refractometer. Their respective accuracies are in the order named. In this connection the specific gravity of anhydrous glycerine should be established, and a reliable table determined or recommended. Of those published, Skalweits and Gerlachs are probably the best.

Organic impurities can be readily determined by igniting a 25-gram portion in a porcelain dish and allowing this to quietly burn off. This is probably as accurate as any method involving heating to a constant weight.

SAMPLING.

The method of sampling is important, particularly on drums containing soap lye and separated salt.

[1] *J. Soc. Chem. Ind.*, **1898**, p. 330.

IN GENERAL.

The committee is in no way bound to the opinions above expressed, and invites the fullest criticism. Even if you are unable to comment on the above problems we should be very glad to receive a simple description in detail of the methods you are using in the analysis and sampling of crude glycerines and dynamite glycerine. Full credit will be given in the committee's report to any suggestions or improvements adopted, unless otherwise desired.

SODIUM FOR DRYING TRANSFORMER OILS.

The Roessler & Hasslacher Chemical Company, selling agents for The Niagara Electro-Chemical Co., manufacturers of metallic sodium, communicated the following information on the drying of transformer oils:

Sodium for Drying Transformer Oils.—Recent experience in connection with the drying of transformer oils has convinced us that by the use of metallic sodium, moisture may be completely removed from oils which are to be used for insulating purposes. This means, of course, that the insulating qualities of the oil will be raised in a very marked. degree.

The method of using sodium for drying hydrocarbon oils is one that is familiar to every chemist who has ever measured the dielectric constants of these oils where the sodium is usually added in the final operation to remove the very last traces of moisture. In the fear that the caustic formed by the reaction of the moisture on the sodium might be left as a liquid or a solid in the hydrocarbon, the chemist has usually thought it necessary to distil off from the sodium. In working on a very large scale this fear has been found to be groundless, and it is absolutely unnecessary to distil the oil.

Properties of Sodium.—Sodium has a density of about 0.97 at 15° C. (39° F.) and melts at 97° C. (207° F.). In transformer oil it will sink unless dragged to the surface by hydrogen gas. With water it reacts to form caustic soda and hydrogen. If very much water is present the caustic soda dissolves and in the presence of oil forms a second layer. If very little water is present the caustic soda is formed on the surface of the metallic sodium and may be removed when removing the sodium. When the sodium surface becomes covered with caustic, it is advisable to remelt under oil, not letting the temperature rise above 120° C. (248° F). After cooling and getting in the shape desired, it is again ready for use for drying more oil. Sodium should always be kept under a good transformer oil.

Method of Use of the Sodium.—One method which we have used with our own transformer oils has been the following:

The oil on the granulated sodium is poured off and a good transformer oil poured over the metal. To the oil which is to be treated, and which is put into an open tank or barrel, the sodium is added at first very carefully, about one ounce to the barrel. If much hydrogen is evolved, this will be conclusive proof that there is much water in the oil, and the balance of the sodium should be added carefully and in small amounts. The amount which is to be added depends upon the oil, but as a rule one pound to the barrel is usually much more than is required. The oil is then stirred up three or four times a day for a minute at a time. After several days the oil may be removed and tested, but the longer it remains over the sodium the better the oil becomes.

Another method used is to put the sodium in the form of sticks in a cylinder of iron wire of about 28 mesh and hang the cylinder in the oil. This method may be used directly with the static which is in use, the only precautions required being those familiar to all electricians in the avoidance of short circuits.

Results.—We have repeatedly taken oils which broke down at 3,000 volts and by letting them stand over the sodium for two days have brought their breaking points up to 20,000 volts or higher Results as good as this had been obtained on a large scale by one of the largest power companies.

STANDARDIZED SAMPLES.

THE SOLVAY PROCESS COMPANY,
SYRACUSE, N. Y., February 17, 1909.

Mr. W. D. Richardson, Editor,
Journal of Industrial and Engineering Chemistry,
4306 Forrestville Ave., Chicago, Ill.

DEAR SIR: The editorial in your last number by W. C. Ebaugh upon Standardized Samples appeals to me strongly. It appears that standardized samples of many important materials are already obtainable, but if this work is undertaken by a committee of industrial chemists, I would like to suggest that standardized samples of Bituminous Coal and Coke be the first to be considered. The coal samples might represent perhaps four types, *viz.*, Pocahontas, Pittsburg Gas, Clearfield and an Illinois or Indiana Coal. These coal samples should be ground to pass a 100-mesh sieve and be standardized particularly as regards volatile matter, sulphur, phosphorus and calorific value. Two coke samples perhaps representing a good by-product and Bee Hive coke should be standardized as regards sulphur and phosphorus content.

It may be urged that coal samples change but if care is taken in keeping the samples the change is almost inconsiderable even as regards calorific value and volatile matter in samples which have been stored several years and absolutely uninfluenced as regards sulphur and phosphorus in either coal or coke. It is, however, the two last constituents mentioned which cause the greatest number of controversies,

Yours truly,
L. C. JONES,
Laboratory Manager,
The Solvay Process Co. and Semet-Solvay Co.

ILLINOIS FUEL CONFERENCE.

The Fuel Conference held at the University of Illinois, March 11th to 13th at Champaign-Urbana, had for its main purpose the bringing together of mine operators, inspectors, bosses and others directly interested in the coal mining industry, for the purpose of inaugurating the work of the Mine Explosion and Mine Rescue station just established at the University. This station is intended to serve the contiguous states of Indiana, Kentucky, Iowa, Missouri and Michigan, by giving instruction to those who may be detailed from the various mining centers, in the use of the oxygen helmets and other devices used in rescue work. This is the first substation to be established after the main one at Pittsburg, which has recently been put in operation.

The success of the Conference was indicated by the very large attendance, about 150 men being present. The pro-

gram covered a much wider scope than the mere presentation of the work and plans of the Rescue Station, about half the time being devoted to topics of more especial interest to the operators and mine inspectors. The other half of the sessions took up the more technical subjects of conservation, the technical and smokeless use of fuel and the methods employed in analytical work.

One immediate result of the Conference was a sudden realization of the fact on the part of the mining men especially, that Illinois, with her very extensive mining interests, had no medium for training experts in this line which more than ever is calling for expert knowledge and technical skill. As a result, a strong memorial was adopted for presentation to the Legislature now in session, praying for the establishment of a department or school of mining engineering at the State University.

The program of the Conference was as follows:

THURSDAY, MARCH 11

First Session—Dr. W. F. M. Goss presiding.

Mechanical Engineering Laboratory.

Formal opening of the United States Geological Survey's Urbana Laboratory for Mine Accident and Mine Rescue Work.

2:00 P.M.—Address of welcome on behalf of the University, President Edmund J. James, University of Illinois. Responses, J. A. Holmes, representing United States Geological Survey; G. W. Traer, representing Illinois Coal Operators; John H. Walker, representing United Mine Workers.

3:30 P.M.—Demonstration in use of the oxygen helmets and in resuscitation work, R. Y. Williams, Mining Engineer, United States Geological Survey.

Second Session—Mr. G. W. Traer presiding.

Physics Lecture Room, Engineering Building.

8:00 P.M.—Address—"Mine Explosions: What the United States Geological Survey Is Doing to Prevent Them." J. A. Holmes, Chief of Technologic Branch, United States Geological Survey.

Address—"The Work of Foreign Mine Explosion Stations." G. S. Rice, Mining Engineer, United States Geological Survey.

Address—"Coal Mining in the United States." E. W. Parker, Statistician, U. S. Geological Survey.

Reception.—At the conclusion of this session the Faculty of the College of Engineering will give an informal reception to the visiting members of the conference.

FRIDAY, MARCH 12.

Third Session—Mr. Richard Newsam presiding.

Lecture Room, Chemistry Building

9:30 A.M.—Address—"The Origin of Coal." (Illustrated.) W. S. Bayley, Associated Professor of Geology.

Address—"The Chemistry of Explosives." C. W. Balke, Associate in Chemistry.

Conference—"Mine Explosions and Their Causes." James Taylor, State Mine Inspector, Illinois; James Epperson, Chief Mine Inspector, Indiana; Joan Verner, State Mine Inspector, Iowa; Carl Scholz, President Coal Valley Mining Co.

12:45 P.M.—Complimentary Buffet Lunch at University Club House.

Fourth Session—Professor L. P. Breckenridge presiding.

Assemble—Mechanical Engineering Laboratory.

2:00 P.M.—General inspection of the laboratories of the University.

Physics Lecture Room, Engineering Building.

3:00 P.M.—Conference—"Smoke Suppression." Paul P. Bird, Chief Smoke Inspector, Chicago; W. A. Evans, Commissioner of Health, Chicago; H. W. Weeks, Fuel Engineer; A. Bement, Consulting Engineer, Chicago; L. P. Breckenridge, Director Engineer Experiment Station.

Fifth Session—Professor S. W. Parr presiding.

Physics Lecture Room, Engineering Building.

8:00 P.M.—Address—"First Aid Work in the Anthracite Mines" H. H. Stoek, Editor, *Mines and Minerals.*

Address—"The College of Engineering and the Mining Interests." W. F. M. Goss, Dean of the College of Engineering.

Address—"The Work of the University of Illinois Engineering Experiment Station." L. P. Breckenridge, Director of the Engineering Experiment Station.

Conference—"Economy in the Use of Fuel for Industrial and Domestic Use." A. Bement, Consulting Engineer, Chicago; D. T. Randall, Engineer, Technologic Branch U. S. G. S.; R. H. Kuss, Assistant Smoke Inspector, Chicago; Edward H. Taylor, Fuel Engineer, Chicago; J. M. Snodgrass, in charge Fuel Investigations, Engineering Experiment Station.

SATURDAY, MARCH 13.

Sixth and Closing Session—Dr. U. S. Grant presiding.

Lecture Room, Chemistry Building.

9:30 A.M.—Address—"The United States Geological Survey and the Fuel Resources of the Country." George Otis Smith, Director United States Geological Survey.

Address—"The Illinois State Geological Survey and the Fuel Interests of the State." H. F. Bain, Director State Geological Survey.

Address—"Coal Analysis." N. W. Lord, Director of the School of Mines, Ohio State University.

For the benefit of those who are unable to attend Thursday, demonstrations of the rescue apparatus will be given each day by Mr. R. Y. Williams.

The United States Geological Survey acting in coöperation with the Illinois State Geological Survey and the University of Illinois has established a Mine Explosion and Mine Rescue Station at Urbana, Illinois. The purpose of the Station is to interest some mine operators and inspectors in the economic value of such modern appliances as the oxygen helmets and resuscitation apparatus as adjuncts to the normal equipment of mines. The Station also will concern itself with the training of mine bosses and others in the use of such apparatus. Its service is to be rendered gratuitously, and so far as possible to all in Illinois, Indiana, Michigan, West Kentucky, Iowa and Missouri, who may desire the benefits thereof.

BOOK REVIEWS AND NOTICES.

Wood Products, Distillates and Extracts. By P. Dumesny and J. Noyer. Translated from the French by Donald Grant. Introduction, xvi pages. Body, 320 pages. London: Scott, Greenwood and Son. New York: D. Van Nostrand Company. Price, $4.50 (net).

Few books have been written giving definite information as to the methods employed in the recovery of technical products from wood, most of such material being scattered, and largely in periodical literature. This book, though giving an account of foreign practice, will nevertheless be welcomed by chemists and others interested in the industries built about the various products of wood distillation, or materials produced from it by other chemical means.

The book is divided into two distinct parts, the first relating essentially to distillates, and the second essentially to extracts.

Part I consists of 127 pages, and it, in turn, is divided into five chapters and an appendix, and is principally confined to a description of products obtained during the destructive distillation of wood, methods for obtaining them, descriptions of apparatus, and the analytical methods employed in determining their purity.

It is interesting to note the absence of any reference to turpentine, or any similar product, as resulting from the destructive distillation, except as inserted by the translator from Circular No. 36, of the United States Department of Agriculture. It would seem, therefore, that this growing industry has received little attention, thus far, abroad. Much space is given to the description of processes for the recovery of pyroligneous acid, to the manufacture and refinement of acetic acid from the crude acetates, and to the making of various acetates. The recovery and purification of wood alcohol also is fully treated. Several pages are devoted to the secondary products, such as oxalic acid, acetone, tar and creosote, and to the manufacture of briquettes from charcoal is touched upon. The recovery of potash from ashes is also dealt with briefly. Some fifteen pages are devoted to a description of the analysis of raw materials and finished products.

An interesting description of processes suggested and attempts to recover products from olive oil residue, especially in Spain, is given in the appendix.

The method and apparatus described for the distillation of wood, and the refinement of products are those ordinarily employed for the harder woods, and do not vary materially from the American practice, but the authors are evidently not familiar with the practice of distillation applied to "fat" wood, as carried out in this country.

Part II, 179 pages, deals with the manufacture and testing of tan-wood extracts, and the utilization of their products in modern tanneries. Some space is given to the general discussion of the effects of deforestation and the importance to industry in the maintenance of the supply of trees capable of yielding tanning material. In view of the recent congress for the discussion of the conservation of our American natural resources, it is interesting to note the warning: "The chestnut tree will disappear from France, if the tannic acid industry continues to fire upon it with red hot bullets." And take heed. The statistics in this book are worthy of careful study.

The description of plant and equipment for treating chestnut wood, the chemical control of the process, commercial details, connected with the operation of the factory and the conduction of the business of manufacturing chestnut extract is exhaustive.

A short chapter of five pages is devoted to the use of chestnut extracts in tanning. Chapter VI describes the manufacture and use of oak extract. Eleven pages, Chapter VII, treat with the same treatment of quebracho extract: Khaki as a substitute for quebracho is also described. Some twenty pages are given to a description of the manufacture and uses of various other tanning substances, dividivi, valonia, Chinese galls, etc. The manufacture of logwood extracts follows.

The last chapter describes the official methods of the International Association of Leather Chemists for the analysis of tanning substances.

The work is well indexed and well illustrated. The printing is clear, on good paper, and the text is amplified by means of useful tables of analyses and other data.

William Hoskins.

Rapid Methods for the Chemical Analysis of Special Steels, Steel-making Alloys, and Graphite. By Charles Morris Johnson, Chief Chemist of the Park Steel Works of the Crucible Steel Company of America. First edition, pages vi+217. New York: John Wiley & Sons. 1909. Price, $3.00.

For contents, "List of Papers" is given. The book is divided into chapters as follows: I. Qualitative Tests for Chromium, Vanadium, Copper, Titanium, Nickel, Molybdenum and Tungsten in Steel, 3 pages. II. Analyses of Vanadium Steel and Ferro-Vanadium, 34 pages. III. Analysis of Titanium Steel and Ferro-Titanium, 16 pages. IV. Analysis of Tungsten Powders. Analysis of Tungsten Steel and Chrome Tungsten Steel. Analysis of Low Per Cent. Tungsten Steel, 13 pages. V. Analyses of Molybdenum Powders. Analysis of Tungsten-Molybdenum Steels, 19 pages. VI. Analysis of Ferro-Chrome, Chrome Ore and Carbonless Chrome, 7 pages. VII. Determination of Aluminium in Steel, 3 pages. VIII. Determination of Copper in Steel and Pig Iron. Separation of Nickel and Copper from Iron and Vanadium by Potassium Ferricyanide. Determination of Copper in Metallic Copper, 15 pages. IX. Rapid Determination of Nickel in the Presence of Chromium, Iron and Manganese, 12 pages. X. Analysis of Ferro-Manganese. Rapid Volumetric Method for Manganese in the Presence of Iron, Calcium and Magnesium, 16 pages. XI. Determination of Carbon in Iron and Steel by Direct Ignition with Red Lead or Litharge. Determination of Carbon in Steel, Ferro-Alloys, and Plumbago by Means of an Electric Combustion Furnace. Also by Gas and Blast, 27 pages. XII. Carbon in Steel by Color. Phosphorus in Steel, Pig Iron, Bar Iron and Wash Metal. Sulphur in Steel, Bar Iron, Pig Iron and Wash Metal. Manganese in Special Steels, Bar Iron and Wash Metal. Silicon in Iron and Steel, 26 pages. XIII. Analysis of Graphite and Graphite Crucibles, 11 pages. XIV. The Annealing of Plain and Special Steels, 9 pages. XV. Percentage Reduction of Acids, 6 pages. XVI. A Practical Automatic Steam Water Still. A Simple Laboratory Method for Making Clay Combustion Boats, 6 pages.

This work is a collection of analytical methods for the detection and estimation of the metals used in making special steels and steel alloys. Methods are also given for the determination of carbon in iron, steel and graphite. The methods given are those used by the author in actual control work of operations, and are based on results obtained from a large amount of experimental data covering years of experience. They are practical in their nature, and the directions for manipulations are clear, concise and well detailed.

The chapters on the determination of carbon in iron and steel by direct ignition and use of the electric furnace are worthy of special mention. The author's opinion of color carbon is given in the first sentence of the chapter of that title, which states: "The determination of carbon by color methods should be indulged in as little as possible." This statement, coming from such authority, may be a surprise to many; but, to the initiated, it is a corroboration of his own ideas, perhaps never expressed publicly.

The preface calls attention to 15 new features and the reader is not disappointed when he reads them in the subject-matter. The book is written by a technical man, and is designed for technical chemists who are called upon to make rapid analyses of such materials as the title embodies. To such chemists the book will prove of inestimable value, since the scientific and technical literature on these subjects is limited and not always easily accessible.

WILLIAM BRADY.

A Short Handbook of Oil Analysis. By AUGUSTUS H. GILL, S.B., Ph.D. Fifth edition, revised and enlarged. pp. 179. Philadelphia and London: J. B. Lippincott Co. 1909. Price, $2.00 net.

Professor Gill's excellent and well-known handbook of oil analysis has reached a fifth edition, which testifies to its general usefulness. In this edition, the changes include a description of the now universal viscosimeter, improved method for antifluorescents and of applying the spontaneous combustion test. Those parts of the book on the detection of animal and vegetable oils, and the treatment of unsaponifiable matter have been entirely rewritten. A new chapter on waste fats and oils has been added, also a description of the titer test, another method for determining sulphur in burning oils and some new tables. For a well-condensed work on the analysis of oils, the present volume can be heartily recommended.

W. D. RICHARDSON.

Heat, Energy and Fuels. By HANNS V. JÜPTNER. Translated by Oskar Nagel, Ph.D. 8vo. pp. 306. New York: McGraw Pub. Co. Price, $3.00 net.

This work is a translation of the well-known volume by Hanns v. Jüptner and is well adapted to the needs of Universities and Engineering Schools, as well as to those of practicing engineers. The subject is treated not only theoretically and practically but details of the latest practice are given. In particular, the measurement of high temperatures, incomplete combustion, combustion temperatures, combustion at constant volume and constant pressure are ably discussed from the theoretical and practical standpoint. Recent data on the melting points of various substances and on solid, liquid and gaseous fuels and their production, and on the gasification of fuels is given. The volume is made up of twenty-five chapters. The work of the translator is well done.

W. D. RICHARDSON.

The Semi-annual Scientific and Industrial Bulletin of Roure-Bertrand Fils, of Grasse, for the fall 1908 has just been issued, on account of delays in preparing special matter for the volume. Under the head of scientific work is given an interesting article on the Essential Oils at the International Congress for the Suppression of Adulterations, Geneva, 1908, by M. Em. Perrott. Under Contributions to the Study of Essentials Oil are detailed six studies of different oils, giving the various constants. The review of recent work on the essential oils occupies 100 pages, or two-thirds of the volume.

NEW BOOKS.

Practical Sheet and Metal Plate Work. By EVAN A. ATKINS. New York: Macmillan Co. 491 pp., over 100 ill., cl. Price, $2 net.

Laboratoriumstechnik. Bibliothek der gesamten Technik. By O. BENDER. 108 Band. Verlag Dr. Max Jänecke, Hanover. Price, Brosch., M., 2.60; geb., M. 3.

Methods for the Analysis of Maple Products and the Detection of Adulterants, Together with the Interpretation of the Results Obtained. By ALBERT HUGHES BRYAN. Wash., D. C., U. S., Office Sup. of Documents 1908 (1909). 13 pp., 8°. (U. S. Dept. Agr., Bureau Chem., Circular). pap. Price, 5c.

The Gases in Rocks. By ROLLIN T. CHAMBERLAIN. Washington, D. C.: Carnegie Inst. 80 pp. Price, 50c.

Die technische Entwickelung der Schwefelsäurefabrikation und ihre volkswirtschaftliche Bedeutung. By E. DROSSER. Verlag von W. Klinkhardt. Leipzig. 1908. 220 Ss., M. 450. Preis, Brosch., M. 12.

Untersuchung und Nachweise Organischer Farbstoffe auf spectroskopischem Wege. By JAROSLAV FORMANEK. Zweite aufl. Erster Theil. Mit 19 Textfiguren und 2 lithogr. Tafl. Berlin: Springer, 1908. viii + 258 Ss.

A Short Hand-book of Oil Analysis. By HERMAN A. GILL. Phila.: Lippincott. 1909. 5th ed., rev. and enl. 179 pp., figs., tabs., cl. Price, $2 net.

Das Ammoniak und seine Verbindung. By Dr. J. GROSSMAN. Helle a. d Saale: Verlag v. Wilhelm Knapp, 1908. Preis, geh., M. 3.60

Metallic Alloys: their Structure and Constitution. By G. H. GULLIVER. London: Charles Griffin & Co., Ltd. 1908.

Natural Sources of Water. By ROB. S. HALL. New York: D. Van Nostrand Co. Cloth. Price, $2 net.

Seifenindustrie-kalender 1909. By O. HELLER. 2 Teile. Leipzig: Verlag Eisenschmidt & Schulze.

Elementary Agricultural Chemistry. By HERBERT INGLE. A Handbook for Junior Agricultural Students and Farmers. Chas. Griffin & Co., Ltd., Exeter St., Strand, London. 1908. Price, 4s. 6d.

Rapid Method for the Chemical Analysis of Special Steels, Steel-making, Alloys and Graphite. By C. MORRIS JOHNSON.

New York: John Wiley & Sons. 1909. 7 + 24 pp., 8°. Price, $3.

Heat Energy and Fuels: Pyrometry, Combustion, Analysis of Fuels and Manufacture of Charcoal, Coke and Fuel Gases. HANS V JÜPTNER, tr. by OSKAR NAGEL. New York: McGraw Publ. Co. 1908 (1909). 5 + 306 pp., figs. Price, $3 net.

Electrometallurgy. By J. B. C. KERSHAW. New York: D. Van Nostrand Co. Cloth. Price, $2.00 net.

Text-book of Botany and Pharmacognosy. By HENRY KRAMER. Phila. and London: J. B. Lippincott Co.

Die Verwertung des Kalis in Industrie und Landwirtschaft. By DR. PAUL KRISCHE. Halle a/S.: Wilhelm Knapp's Verlag. 1908. Price, M. 5.70.

Die Stearinfabrikation. By BÉLA LACH. Halle a/S.: Wilhelm Knapp's Verlag. 1908. Price, M. 6.40.

Examination of Water for Sanitary and Technical Purposes, by Chemical and Bacteriological Methods. H. LEFFMAN. Phila.: P. Blakiston's Sons & Co. 1909. 6th ed., rev. and enl., ill., cl. 144 pp., diags., 12°. Price, $1.25.

Manual of Reinforced Concrete and Concrete Block Construction. By C. F. MARSH and W. DUNN. New York: *Eng. News.* 290 pp., ill. Price, $2.50 net.

Mineral Resources of the U. S.: Pt. I, Metallic Products. Pt. II, Non-metallic Products. 1600 pp., maps. Statistics for 1907, and a résumé of the conditions under which the mineral industries were conducted.

The Mechanical Appliances of the Chemical and Metallurgical Industries; A Complete Description of the Machines and Apparatus Used in Chemical and Metallurgical Processes for Chemists, Metallurgists, etc. By OSKAR NAGEL. New York: Oskar Nagel, P. O. Box 385. 1908 (1909). 7 + 311 pp., diagrs., 8°, ill., cl. Price, $2.00 net.

Elektrolytische Zähler. By DR. KONRAD NORDEN. Halle a/S.: Wilhelm Knapp's Verlag. 1908. Price, M. 9.00.

Clays, Their Occurrences, Properties, and Uses; with Especial Reference to those of U. S. By HEINRICH RIES. 2d ed., rev. New York: John Wiley & Sons. 1908 (1909). 19 + 554 pp., ill., pls., maps, tabs., diags., 8°, cl. Price, $5.00 net.

Microscopic Physiography of Minerals and Rocks. Vol. 2, Massive and Eruptive Rocks. By H. ROSENBUSCH. 4th ed., pp. 717–1592, plates.

Glass Manufacture. By WALTER ROSENHAIN. New York: D. Van Nostrand Co. 264 pp., ill., cl. Price, $2.00 net.

Pharmaceutic Chemistry. By I. V. STANLEY STANISLAUS, M.D., and C KIMBERLY. Phila.: P. Blakiston's Son & Co. 1909. 12°. Price, $2.50 net.

Iron and Steel. By J. H. STANSBIE. New York: D. Van Nostrand Co. 1908. Price, $2.00 net.

Stereochemie. By A. W. STEWART. Deutsche Bearbeitung v. Dr. KARLE LÖFFLER. 87 Textfiguren. Berlin: Springer. 1908. xvi+479 Ss. Preis, Brosch., M. 12.; geb., M. 14.50.

Tonindustrie Kalender, 1909. In three parts. Verlag der Tonindustrie-Zeitung, Berlin. N. W. 21. Price for all three parts, M. 1.50 without postage. Single parts, M. 1 each.

PERSONAL NOTES.

Mr. Paul N. Clancy, of Syracuse, N. Y., Chemist and Engineer of Tests, was last month elected by the Board of Directors of the Clancy Hardward Iron and Steel Co. of the same city to the position of Vice-president of the above-named Company.

Past President Marston Taylor Bogert delivered an address before the American Philosophical Society at Philadelphia, March 19th.

Dr. Edward Ellery, professor of chemistry in Union College, was married on February 20th, to Miss Adelaide F. True, of Waterville, Maine. Dr. Ellery expects to pursue research work in chemistry in the University of Berlin during a five months' leave of absence. Mrs. Ellery will accompany him.

Mr. Henry Bausch, Vice-president of the Bausch and Lomb Optical Company, died at Augusta, Ga., on March 2nd, after a long and painful illness, at the age of fifty years.

After an illness of only a few days' duration, Mr. Geo. J. Seabury, president of the firm of Messrs. Seabury and Johnson, of New York, died Feb. 13th. Born in New York, Nov. 10, 1844, he served one year in the Army of the Potomac; returning to New York he entered the employment of the firm of Hallett, Seaver and Burbank, wholesale druggists. In 1873 he founded the firm of Seabury and Johnson, branching out into the manufacture of rubber adhesive medicinal plasters, extending this to medicated gauzes, cottons and various other pharmaceutical specialties. In 1885 Mr. Johnson retired from the firm and since this time, Mr. Seabury has managed the business alone. His activities in pharmaceutical interests were varied and influential. He was also a voluminous writer on economics, trade, political and public questions. The funeral services took place Feb. 16th, at Orange, N. J.

Dr. R. D. Hall has resigned as Instructor in Analytical Chemistry in the University of Wisconsin to take charge of the analytical and research work of the Westinghouse Lamp Co., of Bloomfield, New Jersey.

INDUSTRIAL AND TRADE NOTES.

It was announced on February 24th that President Roosevelt had denied the petition of the rectifiers which asked for a modification of the internal revenue branding regulations on the misbranding of neutral spirits mixed with whiskey and colored with caramel. He also declined to approve the recommendation of a commission appointed by himself which reported to him in favor of the rectifiers' request. The President endorsed and made public an opinion of Attorney-general Bonaparte, which declares the position of the rectifiers and the conclusions of the commission to be an error. Dr. Wiley's views on whiskey thus are upheld. The attorney-general in declaring that "imitation whiskey" is the only proper name, and in deciding that the terms suggested by Dr. Dunlap are not legal, says:

"I cannot fail to recognize in Dr. Dunlap's recommendation a challenge of the correctness of my conclusions." Mr. Bonaparte declares that the terms suggested by Dr. Dunlap and the rectifiers are not only at variance with the opinions of the Department of Justice, but are also at variance with the decision of the courts."

A bill has been introduced into Congress by Hon. James R. Mann, of Illinois, which requires all packages of foods, drugs, medicines and liquors shipped in interstate commerce to be plainly marked with the net quantity of the contents of the package in terms of weight, measure or numerical count. The measure is in the form of an amendment to the pure-food and drugs act and provides for rules and regulations governing changes from natural causes.

The American Institute of Mining Engineers met in New Haven, Conn., February 23rd and succeeding days. The conservation of natural resources was one of the principal topics discussed.

On March 10th, the Standard Oil Company of Indiana was acquitted of the charges against it by the jury in the second trial on Judge A. B. Anderson's instructions.

Guayule Factory Concession in Mexico.—Consul T. W. Voetter, of Saltillo, advises that an issue of the *Periodice Oficial* of the Mexican State of Coahuila, states that a concession has been granted to Robert L. Bonnet and Eric Notholt by which $10,000 gold is to be invested in a factory for the extraction of rubber from the guayule plant at Nadadores, Coahuila, and which will be exempted from the payment of state and municipal taxes for the period of five years. The concessionaires are obligated to continue the operation of the factory for a further period of five years after the free term, and must deposit a sum of $750 gold in the state treasury as a guaranty fund.

Héroult Furnaces for the United States Steel Corporation.—A most significant point in the development of the steel industry is the adoption of the Héroult furnace by the United States Steel Corporation. Present plans contemplate the construction of two 3 electrode, 15-ton furnaces, one to be installed at the Illinois Steel Company's Works at South Chicago, and the other at the Washburn and Moen Plant at Worcester of the American Steel & Wire Company.

At South Chicago negotiations have been closed with Mr. R. Turnbull, of St. Catherine's, Ontario, Canada, representative for the Héroult Processes for the furnaces, and work is being pushed on their construction. They will be built by the engineering force of the Steel Corporation at the respective plants, and will be ready for operation by July 1st.

The South Chicago furnace will be used for refining liquid Bessemer steel taken from the converters, in order to make a high-grade rail steel and also car wheels and steel axles.

On the other hand, at the Worcester plant the Héroult furnace will be used for refining open-hearth steel for high-grade wire manufacture.

These 15-ton furnaces adopted by the United States Steel Corporation are the largest which have been constructed up to the present time, previous furnaces of this type having reached a capacity of 8 tons only. If the 15-ton furnaces are successful, the Steel Corporation contemplates building others of larger size.

The Hoskins Manufacturing Company, formerly the Hoskins Company, of Chicago, has opened its new plant and general offices at 453 to 471 Lawton Ave., Detroit, Michigan. Here the Company has an extensive factory, new equipment, and enlarged facilities for making and distributing its established line of Electric Furnaces, Pyrometers and Heating Appliances.

With the reorganization and increase of capital to $500,000.00, the management remains the same as before. The officers of the Company are: Mr. Hoyt Post, *President*; Mr. W. W. Talman, *Vice-president and Sales Manager*; Mr. E. F. Hoskins, *General Manager and Treasurer*; and Mr. Jonathon Palmer, Jr., *Secretary*. Mr. A. L. Marsh will continue in the capacity of Electrical Engineer for the Company.

Water Power Wanted for Air-nitrate Factories.—Representatives of European interests manufacturing air nitrates by hydro-electric power for fertilizers are in the United States to see what can be done in the way of securing large water powers for establishing such factories in this country. An industry of this kind is needed as the imports of Chilean nitrate of soda now amount to $14,000,000 a year. Difficulty is being experienced, however, in securing suitable water powers at reasonable cost. Governments of other countries are said to be offering inducements for the location of the extensive nitrate mills which the company proposes to erect.

Extensive Chemical School Planned in Germany.—Consul-General Richard Guenther, of Frankfort, advises that an association has been formed in Germany for the purpose of establishing a national chemical laboratory. A fund of 1,000,000 marks ($238,000) is to be raised for erecting a suitable building with the requisite equipment. The board of directors of the association is requesting the Federal Government to support the new institution by an annual subvention of 100,000 marks ($23,800). The state Government of Prussia has tendered a site for the building free of cost.

The following statement regarding conditions in the American Portland cement industry during the year 1908 has been prepared by Mr. Edwin C. Eckel for the United States Geological Survey:

Although detailed figures are not yet obtainable, an estimate based on the information available indicates that the production of Portland cement in the United States was somewhat less than 40,000,000 barrels. This compares as follows with the output of recent years:

	Barrels
1905	35,246,812
1906	46,463,424
1907	48,785,390
1908 (estimated)	40,000,000

The falling off from the 1907 output was heavy, and is particularly notable because it is the first decrease shown in any year by the American cement industry since its in-

ception. The decrease was not uniformly distributed throughout the country, for New York, Pennsylvania, and New Jersey will probably show the highest percentages of loss, while in some portions of the West and the Middle West the decrease was relatively slight.

The year 1909 opens with heavy stocks of cement on hand at most mills, but with good prospects for a steady, though slow, revival in the cement trade. It is unlikely that this revival will be sufficiently rapid to push mills to their capacity during the year, and it is therefore possible that the high record for output made in 1907 will remain unbroken for another year at least. The total maximum capacity of existing plants is now about 60,000,000 barrels a year.

Despite the business depression, or perhaps partly because of it, there have been a number of important technical and industrial developments in the cement industry during 1908, and others are still pending. These will be discussed in the Survey's final report on cement production, which will be issued early in the spring.

American Patents in England.—Consul Albert Halstead, of Birmingham, has made a number of inquiries as to the effect upon Birmingham industries of the new British patents and designs act of 1907, which requires foreign patents, if they are to be protected by British patent laws, to be worked wholly or adequately in the United Kingdom. The consul writes:

I have heard it said that many foreign manufacturers, including Americans, were establishing factories in the United Kingdom, or licensing British manufacturers to manufacture patents for them under their patent rights, but have not learned of any Americans locating in this consular district. From inquiries made of me by owners of factory property it would seem that there were plenty of factories that British owners wished to sell or lease to American manufacturers at a good round price.

While there appears to have been no establishment of American factories in this section of England since the act became effective, I learn that a number of British firms are working American patents under royalties. One Birmingham jewelry firm is busy making an American specialty that requires electroplating, whereas most of the Birmingham jewelers are complaining of slack times, and another firm has laid down a special plant to manufacture a certain galvanized-iron article that has not previously been made in England, but is in general use in the United States.

I am also told that other Birmingham firms are profiting through working American patents for American manufacturers, but British manufacturers benefiting from the new British law, and making American patented articles under license, are not disposed to discuss the matter or to advertise their success.

Birmingham manufacturers themselves are not encouraging the establishment of new factories by Americans or other foreigners, because such factories would ultimately compete in other lines as well as in those for which they were especially established, but are encouraging Americans to sell them their patent rights, or to authorize their manufacture under royalties.

Taking the United Kingdom as an entirety, it would seem that the number of American manufacturers who have protected themselves by complying with the provisions of the law is very considerable, and represents a large amount of work taken from American workmen; but there must be a far greater number who have overlooked the importance of so doing, and who are thus risking the forfeiture of their patents and the manufacture of their articles in the United Kingdom by British firms and without compensation, even though their articles have not as yet been introduced into this market, because the British manufacturers are very well contented with the new law and are watching keenly for all such opportunities.
—*U. S. Consular Report*, Feb. 19, 1909.

Tin Plant in Transvaal.—There has just been completed at Groenfontein, near Potgietersrust, in the Transvaal, a plant for dressing tin ore, which Consul Edwin N Gunsaulus, of Johannesburg, describes:

The coarse crushing takes place in a Blake-Marsden rock breaker of the ordinary pattern. From this the ore passes direct to the mill bins, whence it is fed into the mortar boxes of the 10 stamps, each weighing 1,050 pounds and dropping 97 times per minute. The crushed ore passes to a conical hydraulic separator, where the fine stuff passes off at the top through a launder on to a Wilfley table, and the coarser stuff is delivered to two other Wilfley tables. These separate out three grades of stuff, namely, concentrates, middlings, and waste. The Wilfley table separates the heavy and the light grains into layers by agitation, and then by the jerking action throws them toward the head end, and while at the same time the lighter grains are washed down the slope toward the tail side by the surface water, which flows at right angles to the direction of the jerk.

The concentrates are almost entirely of pure cassiterite, and do not require any further treatment. The middlings, which consist largely of particles of tinstone attached to gangue matter, are reground in an auxiliary pulverizing mill. The waste sands pass to two spitzkasten. The coarser stuff from the bottom of the first spitzkasten is treated on a fourth Wilfley table, the finer stuff passing over into the second spitzkasten, the coarser stuff from which is delivered onto two Frue-vanners, while the finer slimes, together with the residues from the fourth Wilfley table and the Frue-vanners, are led away and stored in a dam for future treatment.

The Frue-vanner is essentially a traveling endless belt, which is slightly inclined from the horizontal and receives a rapid shake in the plane of the belt, while at the same time it has a continuous slow motion up the slope. The agitation makes the ore bed so loose that minerals of higher specific gravity can settle to the lower layer, while those of lower specific gravity rise to the upper layer. The travel of the belt carries the heavy minerals to the upper end, and the surface water washes down the light mineral to the lower or tail end. The whole plant is being run by a 60-horse power Tangye suction gas engine and has a capacity of 1,000 tons per month.—*U. S. Consular Report*, Feb. 23, 1909.

Canadian Iron Ore.—Consul-General William Harrison Bradley, of Montreal, furnished the following information concerning a combination of Canadian companies for the

working of iron ores, especially New Brunswick ores, heretofore considered practically worthless:

"The consolidated company is known as The Canada Iron Corporation (Limited), and is formed of four companies formerly owned and operated by Montreal interests. The corporation has an authorized bond issue of \$3,000,000, of which \$2,500,000 is to be issued. Its authorized capital is \$8,000,000, of which \$3,000,000 is 6 per cent. preference cumulative and \$5,000,000 common. Its total assets are about \$11,000,000, according to its own valuation. The company is now negotiating for a short railway line to help them market their ores.

"The head office of the corporation is in Montreal. The location of its foundries and their daily outputs are, in tons: Fort William, Ontario, 150; St. Thomas, Ontario, 100; Hamilton, Ontario, 80; Quebec, 50; Three Rivers, Quebec, 70; Londonderry, Nova Scotia, 50; total finished product, 500 tons. Furnace and daily output in tons: Midland, Ontario, coke iron blast furnace, 125; Radnor, Quebec, charcoal iron, 30; Drummondville, Quebec, charcoal iron, 20; Londonderry, Nova Scotia, coke iron blast furnace, 125; total, 300 tons. Iron ore mines and output per day in tons: Eganville, Ontario, 200; Bessemer, Ontario, 1,000; Annapolis, Nova Scotia, 2,000; Bathurst, New Brunswick, 3,000; total, 6,200 tons."

The following is taken from the report of an American expert, who investigated the mines:

"I consider this mine the most valuable one I have examined in Canada. It is the largest body of iron ore known to me to exist in the Dominion to-day. There are three principal ore-bearing areas that I estimate contain, in the aggregate, 20,000,000 tons of merchantable iron ore (hematite) carrying 53 to 55 per cent. of metallic iron, this estimate being arrived at after rejecting all ore running below this standard.

"If a valuation is made on a royalty basis of one dollar per ton, which is the common price in the United States, and in my opinion a very moderate one in the present instance, on account of the proximity of the mine to the seaboard, the Bathurst property will show at least \$20,000,000.

"The following analysis from No. 1 area (estimated to yield 10,000,000 tons), made by a government analyst, demonstrates the quality of the ore, in percentages: Iron, 62.83; insoluble, 10.39; manganese, 0.624; sulphur, 0.109; phosphorus, 0.735; titanium, none."—*U. S. Consular Report*, March 3, 1909.

German Peat-gas Plants.—Consul-General A. M. Thackara, of Berlin, forwards a translation by Consular Agent W. B. Murphy, in which is discussed the utilization of the extensive peat deposits in Germany for the production of electric power, and, as a side product, of nitrogen fertilizer. The following extract will be of interest:

"A peat-gas plant is being erected near Svedala, Sweden, which will transform power won from peat into electricity, and this electric power will be conducted to neighboring towns for consumption by municipalities and industrial plants. Of the peat used in experiments, 100 kilos (220 pounds) produced about 327 cubic yards of gas at 0° and 760. Peat-gas machines require less than half as much fuel as steam machines for the production of a given amount of power

"Calculations show that from central stations located on the banks of the Ems River, where there are extensive peat deposits, electric power can be produced and conducted to surrounding towns, not only as cheaply as that furnished by the south German water-power plants in Rheinfelden, but at prices that will compete with those charged for power in Scandinavia, Switzerland, and by the Niagara Falls company.

"In order that Germany may not become dependent on foreign countries for manures containing nitrogen, the latent resources existing in the moors of Germany should be developed.

"With a plant of 10,000 horsepower 40 tons of carbide can be produced in twenty-four hours, and 100 parts of carbide with 25 specific parts of nitrogen give 125 parts of manure containing 20 per cent. of nitrogen. It hardly needs to be pointed out that the yearly maximum production of 15,000 tons of manure containing nitrogen, by means of an electric central station of 10,000 horse power, would give German agriculture, which now uses 500,000 tons of Chile saltpeter and 150,000 tons of sulphuric ammonia, a very welcome addition to its by no means sufficient supply of manures.

"Taking as a basis the agricultural-chemical experiments carried out since the year 1901, it can already be considered as indisputable that calcium cyanamide, which is obtained from calcium carbide by admittance of atmospheric nitrogen, constitutes in many cases a useful substitute for the manures containing nitrogen imported from abroad, particularly Chile saltpeter and sulphuric ammonia."—*U. S. Consular Report*, March 8, 1909.

South Sea Phosphate.—Consul Julius D. Dreher, of Tahiti, furnishes the following information concerning the discovery of phosphate on an uninhabited British possession in the South Seas:

"Henderson Island is about 150 miles northeast of Pitcairn Island, and 300 miles east of Gambier Islands, which are in the Tahiti consular district. According to one of the two men who discovered the phosphate, Henderson is an elevated island, several times as large as Makatea, which has an area of some 10 square miles. The preliminary investigations made on various parts of the island show that there are large deposits of phosphate thereon. It outcrops on the land and was found at several places to extend to a depth of 6 feet, which was as low as the examination was made. Specimens analyzed show that some of the phosphate at least is of a high grade. Of the other two islands, Ducie is elevated and it is quite probable that deposits of phosphate will be discovered on it.

"My informant has sent his report and many specimens of the phosphate to London. He informs me that a thorough survey and examination of Henderson will soon be made."—*U. S. Consular Report*, March 12, 1909.

German Viticultural Legislation.—Consul Thomas H. Norton, of Chemnitz, advises that the protection accorded by existing German laws to grape-growing interests is confined chiefly to statutes designed to safeguard the purity of wine. Mr. Norton discusses their provisions and contemplated changes as follows:

The present law came into force on May 24, 1901. Its chief provisions are as follows:

In the law of 1879 regarding foodstuffs, etc., certain forms of adulterated or imitation wines are forbidden. Exception is made in the following cases, where the products of the operation are not to be considered as falsified wines:

"(1) The recognized cellar treatment of wine, including preservative methods, even when alcohol or small quantities of albumen, gelatin, isinglass, etc., tannin, carbonic acid, sulphurous acid, or sulphuric acid formed therefrom, are added for the purpose; however, the amount of alcohol added, in as far as foreign southern or sweet wines are not concerned, should not amount to more than 1 per cent. of the volume.

"(2) Mixing of wine with wine.

"(3) The lessening of acidity by means of pure precipitated calcium carbonate.

"(4) Addition of technically pure cane, beet, or invert sugar, technically pure starch sugar, likewise in aqueous solution, in as far as such additions are made merely for the purpose of improving the wine without materially increasing its amount; further, in character and composition, and especially in the percentage of extractive substances and mineral matter, such sugared wine shall not be inferior to the average grade of the unsugared wine of the vineyard territory to which the wine, according to the designation given it, should correspond."

The industrial production of so-called wines by the following processes is totally forbidden:

"(1) An addition of sugar solution or ordinary water to grapes, grape mash, grapes wholly or partly expressed, mixed with yeast (producing grape wine and yeast wine).

"(2) The use of dried fruits (also their extracts by solvents or by boiling) or concentrated fruit sirups, even though their use is permitted in making beverages which occur in trade as foreign dessert wines.

"(3) Artificial sweetening matters.

"(4) Tartar, tartaric acid, etc., aromatic matters.

"(5) Artificial fruit sirups or essences, even though the use of aromatic and medicinal substances is permitted in making wines which appear on the market in the form of the ordinary root beverages or medicines.

"(6) Cider and fruit wine.

"(7) Gums or other substances by means of which the extractive substance would be increased."

Further it is forbidden to have for sale or to sell wine, to which sugar has been added, so labeled as to give the impression that such addition had not been made. The designations prescribed by the imperial federal council must be given on price lists, wine lists, and other forms of advertisements. The addition of the following to wines, and to beverages resembling wine is forbidden:

Soluble aluminum salts (alum and the like), barium salts, boric acid, glycerin, foxglove, magnesium compounds, salicylic acid, oxalic beginning with the opening of the vintage and ending on January 31st of the following year. During this period wines of earlier vintages may also be treated. The addition of sugar can take place only in the region where the wine is produced. The intention to make use of this permission must be announced to the proper authorities. The addition of sugar to a deteriorated wine to produce a new fermentation requires a special permission of the authorities. Wine growers and wine merchants are required to inform purchasers, if the demand is made, whether the wines in question have received an addition of sugar, and to be thoroughly familiar with the facts in the case. In the labeling of "sugared" wine the character of the grapes used and the year of vintage may be indicated, but it is forbidden to add the name of the wine grower or the region of production.

Geographical designations in the commerce with wines are limited to indicating their origin. The present practice, however, of using such designations for the purpose of distinguishing between similar products of the same region is allowed.

It is totally forbidden to make imitation wines for other than household use, or to import the same. The distinction is drawn between beverages which may replace wine, such as fruit or vegetable juices, malt extracts, etc. (which are permissible), and liquids intended to so closely resemble wine that they may deceptively be sold as such. The imperial council possesses the right to limit the choice of materials from which such beverages may be prepared.

Champagne must be labeled with the name of the land in which the bottles were filled. If the fermentation did not take place in bottles the fact must be indicated on the label. The term "cognac" can be applied only to brandies, the alcohol of which is obtained from grape juice. The land of origin must be placed upon the label.

Each wine grower is required to keep a very complete set of books, showing how much grape juice and how much wine he has produced directly, how much has been purchased from others; the quantity of sugar used and how employed; what liquids similar to wine he has produced or purchased. Dates and names are to accompany all transactions of sale or purchase. Such books must be retained for five years after the last date of entry.

Official experts are to be appointed in each wine district with full powers for inspecting cellars, books, etc. Absolute silence is required in regard to all trade secrets learned during inspection. The execution of the law is entrusted to the various Federal States and their officials. The maximum punishment prescribed is two years' imprisonment and a fine of $4,000.

The whole tenor of the proposed law is in harmony with the dominating principle of the American pure-food law, *i. e.*, the preventing of the sale of wares without full knowledge on the part of the purchaser of just how the food or beverage has been manufactured, and what are its constituents. *U. S. Consular Report*, February 27, 1909.

The second annual Cement Show at the Coliseum, Chicago, February 18 to 24, 1909, was most successful in the number of exhibitors and the variety of exhibits, and the great interest shown by the general public in cement as a structural material. All of the standard makes of cement were represented, as well as the makers of cement machinery. The key-note of the show was the fireproof qualities of cement. Several exhibits of water-proofing processes were to be seen, but there was no great novelty in this direction. One of the most interesting exhibits was that of Robert W. Hunt & Company, engineers of Chicago, of a model testing laboratory. This exhibit contained tensile testing machines of the lever and shot type, a glass top testing table, with a

complete layout of apparatus for the various tests made in connection with the inspection of cement. With their operators in white uniforms and with demonstrations of the various tests, together with informal explanations of their methods of handling the work, their exhibit was valuable and interesting to those directly interested as users of cement, and pleasingly enlightening to those not familiar with the service.

It will probably be interesting to our readers to know that their work is done entirely for the users of cement or for those who specify the use of cement. They test under the standard specifications for cement recommended by the American Society of Civil Engineers. These are embodied in a small pamphlet, which, in addition, contains some very valuable comments on the significance of the different tests. Space does not allow our printing this data here but Robert W. Hunt & Co. state that they will be pleased to send same to any of our readers on request to their main office, 1121 The Rookery, Chicago.

Work was resumed in full March 15th at Mills Nos. 3 and 4 of the Alpha Portland Cement Company at Martin's Creek. Mill No. 3 had been shut down since Christmas and Mill No. 4 since February 13th. Operations were resumed at Mill No. 2 at Alpha, N. J., on March 22nd.

OFFICIAL REGULATIONS AND RULINGS.

Food Inspection Decision 104.

Amendment to Food Inspection Decisions No. 76 and No. 89, Relating to the use in Foods of Benzoate of Soda.—The Referee Board of Consulting Scientific Experts, composed of Dr. Ira Remsen, Dr. Russell H. Chittenden, Dr. John H. Long, Dr. Alonzo E. Taylor, and Dr. C. A. Herter, have reported upon the use of benzoate of soda in foods. The Board reports, as a result of three extensive and exhaustive investigations, that benzoate of soda mixed with food is not deleterious or poisonous and is not injurious to health. The summary of the report of the Referee Board is published herewith.

It having been determined that benzoate of soda mixed with food is not deleterious or poisonous and is not injurious to health, no objection will be raised under the Food and Drugs Act to the use in food of benzoate of soda, provided that each container or package of such food is plainly labeled to show the presence and amount of benzoate of soda.

Food Inspection Decisions 76 and 89 are amended accordingly.

George B. Cortelyou,
Secretary of the Treasury.
James Wilson,
Secretary of Agriculture.
Oscar S. Straus,
Secretary of Commerce and Labor.

The Influence of Sodium Benzoate on the Nutrition and Health of Man.

Of the questions referred to this Board[1] the first to engage our attention have been the following:

(1) "Does a food to which there has been added benzoic acid, or any of its salts, contain any added poisonous or other added deleterious ingredient which may render the said food injurious to health? (*a*) In large quantities? (*b*) In small quantities?"

(2) "If benzoic acid or any of its salts be mixed or packed with a food, is the quality or strength of said food thereby reduced, lowered, or injuriously affected? (*a*) In large quantities? (*b*) In small quantities?"

To obtain satisfactory answers to these questions the Board has felt it necessary to carry through a careful investigation of the effect of benzoic acid or some one of its salts on the nutrition and general health of man. A thorough study of the literature giving the results of work done by various investigators on the physiological effects of benzoic acid and its salts, together with a study of reported clinical and medical observations, therapeutic usage, etc., have made it apparent that additional work was needed to render possible a conclusive answer to the above questions.

With a view to limiting the scope of the work, while at the same time meeting all practical requirements, our investigation, with the consent of the Secretary of Agriculture, has been confined to a study of the effect of the sodium salt of benzoic acid, *viz.*, sodium benzoate.

To make this experimental inquiry as thorough as possible, and to minimize the personal equation, three independent investigations have been carried out—one at the medical school of Northwestern University, in Chicago, under the charge of Prof. John H. Long, of that institution; a second at the private laboratory of Prof. Christian A. Herter, of Columbia University, New York City; and the third at the Sheffield Scientific School of Yale University, in charge of Prof. Russell H. Chittenden.

The same general plan of procedure was followed in all three experiments. A certain number of healthy young men were selected as subjects, and during a period of four months these men, under definite conditions of diet, etc., with and without sodium benzoate, were subjected to thorough clinical and medical observation, while the daily food and the excretions were carefully analyzed, and otherwise studied, and comparison made of the clinical, chemical, bacteriological, and other data collected. (For details, see the individual reports.) In this manner material has been brought together which makes possible conclusions regarding the effect of small and large doses of sodium benzoate upon the human system.

In fixing upon the amount of sodium benzoate that should constitute a "small dose," we have adopted 0.3 gram of the salt per day. Manufacturers of food products, which in their view require the use of a preservative, are in general content with 0.1 per cent. of sodium benzoate. This would mean that in the eating of such a preserved food the consumer would need to take 300 grams per day, or nearly two-thirds of a pound of preserved food to ingest an amount of benzoate equal to our minimal daily dosage. Looked at from this point of view, our dosage of 0.3 gram per day seemed a fair amount for a "small dose," one that would clearly suffice to show any effect that small doses of the salt might exert, especially if continued for a considerable length of time. In all these four experiments this daily dosage was continued for a period of about two months. Under "large dose" was included quantities of sodium benzoate

[1] Dr. Alonzo E. Taylor, Professor in the University of California, a member of this Board, owing to absence in Europe, has not been able to participate in the investigations embodied in this report.

ranging from 0.6 gram to 4 grams per day. Such a daily dosage was continued for a period of one month. In a few instances somewhat larger doses were employed.

As the amount and character of the daily diet exert a well-known influence upon many of the metabolic or nutritive changes of the body, as well as upon the bacterial flora of the intestines, attention is called to the fact that the three investigations differed from each other in the amount of protein food consumed daily, thereby introducing a feature which tends to broaden the conditions under which the experiments were conducted.

The conclusions reached as a result of the individual investigations are given at length in the separate reports herewith presented, together with all of the data upon which these conclusions are based.

The fact should be emphasized that the results obtained from the three separate investigations are in close agreement in all essential features.

The main general conclusions reached by the Referee Board are as follows:

First.—Sodium benzoate in small doses (under 0.5 gram per day) mixed with the food is without deleterious or poisonous action and is not injurious to health.

Second.—Sodium benzoate in large doses (up to 4 grams per day) mixed with the food has not been found to exert any deleterious effect on the general health, nor to act as a poison in the general acceptation of the term. In some directions there were slight modifications in certain physiological processes, the exact significance of which modifications is not known.

Third.—The admixture of sodium benzoate with food in small or large doses has not been found to injuriously affect or impair the quality or nutritive value of such food.

IRA REMSEN, *Chairman*,
RUSSELL H. CHITTENDEN,
JOHN H. LONG,
CHRISTIAN A. HERTER,
Referee Board of Consulting Scientific Experts.

FOOD INSPECTION DECISION 105.

The Labeling of Canned Salmon and White Fish.—Many inquiries have been made of the Department regarding the nomenclature commonly employed in designating canned salmon. It is stated that inferior species of salmon are frequently canned and labeled with some name which is understood by the trade to indicate the presence of fish of an inferior variety but which is not so understood by the consumer; as, for instance, "Alaska Salmon." The Department is informed by the Bureau of Fisheries that the species of salmon in the United States are as follows:

"1. *Oncorhynchus nerka.* Sockeye or sockey salmon, blueback salmon, red salmon, redfish, or nerka salmon.

"2. *Oncorhynchus tschawytscha.* Chinook salmon, king salmon, quinnat salmon, tyee salmon, or spring salmon.

"3. *Oncorhynchus gorbuscha.* Humpback salmon, pink salmon, or gorbuscha salmon.

"4. *Oncorhynchus kitsutch.* Coho salmon, silver salmon, or medium red.

"5. *Oncorhynchus keta.* Calico salmon, keta salmon, dog salmon or chum salmon.

"6. *Salmo gairdneri.* Steelhead salmon, steelhead, hardhead winter salmon, salmon trout, or square-tailed trout.

"7. *Salmo salar.* Atlantic salmon."

Two additional species of landlocked salmon exist in certain New England and Canadian lakes. Neither of these nor the Atlantic salmon is ever canned. Considering this fact, and the further fact that many packers put up humpback and dog salmon under fancy names and thus sell them to consumers who may believe them to be of superior varieties, it is held that canned salmon should be labeled with one of the common names mentioned above as belonging to the species of fish canned.

A similar question has frequently been raised regarding whitefish. A fish designated as *Argyrosomus artedi*, usually called lake herring or cisco, is put on the market at times as "family whitefish." The following is quoted from a communication from the Bureau of Fisheries:

"The whitefish tribe in America has numerous representatives, and at least 12 species are regularly caught for market, and others will doubtless in time acquire economic importance. Those now taken are:

"Common whitefish of Lake Ontario and Lake Erie, *Coregonus albus*; common whitefish of Lake Huron, Lake Michigan, Lake Superior, Lake of the Woods, Lake Winnipeg, etc., *Coregonus clupeiformis*; Rocky Mountain whitefish, *Coregonus williamsoni*; broad whitefish or Alaska whitefish, *Coregonus kennicotti;* Menominee whitefish or round whitefish, *Coregonus quadrilateralis*; Lake herring, or cisco, *Argyrosomus artedi*; jumbo herring, or Erie cisco, *Argyrosomus eriensis*; Huron cisco or herring, *Argyrosomus huronius*; moon-eye, or chub, *Argyrosomus hoyi*; longjaw whitefish, or bloater, *Argyrosomus prognathus*; longjaw, of Lake Superior, *Argyrosomus zenithicus*; blackfin or bluefin whitefish, *Argyrosomus nigripinnis*; tullibee whitefish, *Argyrosomus tullibee.*

"To most of these species the name 'whitefish,' with a qualifying word, is strictly applicable; but there is a wide range in food value, and to permit the sale of most of them as plain 'whitefish' would be unjust to the public. The Bureau does not know that this general question has come before your Board, or that you wish to consider it at this time, but sooner or later it will be necessary to render a decision, and at any time it may be brought to your attention because of cases arising in the Washington (D. C.) market, where one of the commonest and best of the fish food is 'smoked whitefish'—consisting of any one of three or four species of *Coregonus* and *Argyrosomus*, none of them *clupeiformis* or *albus*. Under these circumstances it would appear to this Bureau to be proper and feasible to require the different kinds of preserved whitefish to be designated by their qualifying names. The most appropriate name for 'family whitefish' is lake herring or cisco; but whitefish as here used would mean, or would be intended to mean, the common whitefish, the best of the tribe."

In harmony with the opinion of the Bureau of Fisheries, the Board holds that the term "whitefish" should be applied only to the common whitefishes, *Coregonus albus* and *Coregonus clupeiformis*, unless prefaced by the name of the particular species of whitefish employed. The fishes commonly known to the fisherman and the trade as "lake herring"

and "cisco" should be so called, with or without qualifying names, but should not be designated "whitefish."

H. W. WILEY,
F. L. DUNLAP,
GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved:
JAMES WILSON,
Secretary of Agriculture,
WASHINGTON, D. C., February 17, 1909.

(T. D. 29546) *Adeps lanae.*—ZINKEISEN *v.* UNITED STATES.—U. S. Circuit Court of Appeals, Second Circuit. January 12, 1909. No. 119 (suit 4920).

ADEPS LANAE—MEDICINAL PREPARATION—WOOL GREASE

"Adeps lanae anhydrous and adeps lanae cum aqua, which are worth from 10 to 15 cents per pound, are used principally in therapeutics and generally sold to the drug trade, though used to some extent in medicinal soaps and salves, are not 'wool grease' within the meaning of paragraph 279, tariff act of 1897, but 'medicinal preparations' under paragraph 68."

APPEAL from the circuit court of the United States for the southern district of New York.

(Decision in favor of the Government.)

The decision below (T. D. 29000) affirmed a decision by the Board of United States General Appraisers, Abstract 15013 (T. D. 28074), which had overruled protests of Zinkeisen & Co. against the assessment of duty by the collector of customs at the port of New York. The article in controversy was invoiced as "adeps lanae anhydrous," "adeps lanae cum aqua," and "wool grease."

Walden & Webster (*Howard T. Walden* of counsel), for the importers.

J. Osgood Nichols, Assistant United States Attorney, for the United States.

Before LACOMBE, COXE, and NOYES, Circuit Judges.

On appeal from a decision of the circuit court for the southern district of New York, which affirmed the decision of the Board of General Appraisers sustaining the action of the collector in assessing the merchandise in controversy as medicinal preparations under paragraph 68 of the tariff act of 1897.

COXE, *Circuit Judge*: The collector classified the appellants' importations under paragraph 68 of the act of 1897, which reads as follows:

"Medicinal preparations not containing alcohol or in the preparation of which alcohol is not used, not specifically provided for in this Act, twenty-five per centum ad valorem; calomel and other mercurial medicinal preparations, thirty-five per centum ad valorem. (30 Stat., 154)."

The appellants insist that their merchandise should have been assessed as "wool grease" under paragraph 279 of the same act, which is as follows:

"Tallow, three-fourths of one cent per pound; wool grease, including that known commercially as degras or brown wool grease, one-half of one cent per pound. (30 Stat., 172)."

The Board and the circuit court, after a careful review of the facts, reached the conclusion that the merchandise was not wool grease. If not wool grease, the appellants must fail.

In February, 1895, two years prior to the passage of the act in question, the circuit court, in Movius *v.* United States (66 Fed. Rep., 734), had before it a case in all essential particulars similar upon the facts to the case at bar. The paragraph (316) of the act of 1890 was identical in language with the paragraph now in question. The court there described wool grease as follows:

"Wool grease is of a brown color and viscous consistency. It is extracted from wool washings, and consists of cholesterin and other fats and volatile fatty acids. It contains from 15 to 30 per cent. of potash. It emits a rank, disagreeable odor, it resembles molasses and tar mixed together, it is imported in returned petroleum barrels, it is worth from 2½ to 3 cents a pound, and its chief use is for stuffing leather."

The merchandise in question here is a highly finished product, used principally in therapeutics, and is sold generally to the drug trade, but a portion thereof (represented by Sample 3 and 4) is used for medicinal and very high-class soap and for salves, imparting thereto certain curative properties. It is worth from 10 to 15 cents per pound. It is not wool grease chemically, is used for entirely different purposes, and has never been known commercially as wool grease or degras.

We think that the importations are medicinal preparations as that term has been defined by the courts, and that there is no satisfactory testimony that it is possible to use them otherwise. Dodge *v.* United States (130 Fed. Rep., 624; T. D. 25240); Park *v.* United States (66 Fed. Rep., 731).

The case is stronger for the Government than the Movius case, for the reason that the court prior to the passage of the present act had construed "wool grease" to include only the crude raw material and not the refined and expensive products derived therefrom. With this construction presumably in mind, Congress reenacted the paragraph in identical language. This would hardly have been done if Congress had intended that the refined and expensive "lanolin" should enter as wool grease and pay duty at the rate of only one-half of 1 cent per pound.

The decision is affirmed.

(T. D. 29547) *Zinc Ores.*—UNITED STATES *v.* BREWSTER.—U. S. Circuit Court of Appeals, Fifth Circuit. January 18, 1909. No. 1811 (suit 1961).

ZINC ORES—CALAMINE—CRUDE MINERALS—CARBONATE, SILICATE AND SULPHIDE OF ZINC—LEAD-BEARING ORES.

"The zinc ores known as carbonate, silicate, and sulphide of zinc are free of duty under the tariff act of 1897, the carbonate and silicate as 'calamine' under paragraph 514, and the sulphide as 'minerals, crude,' under paragraph 614, except that when containing lead the lead contents are subject to the duty provided in paragraph 181 on 'lead-bearing ore of all kinds.'"

APPEAL from the circuit court of the United States for the southern district of New York.

(Decision adverse to the Government.)

The decision below (T. D. 29006) affirmed decisions by the Board of United States General Appraisers, Abstracts 14438–9 (T. D. 27937), which, on the authority of *In re* Cockerill Zinc Company, G. A. 6540 (T. D. 27891), reversed the assessment of duty by the collector of customs at the port of Laredo.

The case involves the following paragraphs of the tariff act of 1897.

"PAR. 181. Lead-bearing ore of all kinds, one and one-half cents per pound on the lead contained therein. * * *

"PAR. 183. Metallic mineral substances in a crude state, and metals unwrought, not specially provided for in this Act, twenty per centum ad valorem. * * *

"PAR. 514. Calamine. (Free).

"PAR. 614. Minerals, crude, or not advanced in value or condition by refining or grinding, or by process of manufacture, not specially provided for in this Act. (Free)."

The character of the materials in controversy is stated as follows in the Government's brief:

"The imported ores, broadly described, were:

"(*a*) Concentrated sulphides containing 28 per cent. zinc and 2 per cent. lead.

"(*b*) Carbonates crushed and hand-picked, containing 28 per cent. zinc and 7 per cent. lead.

"(*c*) Carbonates and silicates combined, crushed and hand-picked (21 to 35 per cent. carbonate, 2 to 26 per cent. silicate), in some less than 1 per cent. of lead, and in others no lead."

In some instances duty was assessed under said paragraph 183, tariff act of 1897; in other instances duty was assessed on the lead contents under said paragraph 181, and on the zinc contents under paragraph 183; and in one case duty was assessed only on the lead contents.

The Board of General Appraisers held, as claimed by the importer, that the merchandise was free of duty, the carbonates and silicates under paragraph 514, as "calamine," and the sulphides under paragraph 614, as "minerals, crude." This conclusion was affirmed by the circuit court.

Lodowick McDaniel and *Rufus E. Foster*, United States attorneys (*James C. McReynolds*, special assistant to the Attorney-General, of counsel; *Charles E. McNabb* on the brief), for the United States.

Baker, Botts, Parker & Garwood (*W. Wickham Smith* of counsel; *Henry S. Wardner* and *Howard T. Walden* on the brief), for the importer.

Before PARDEE, McCORMICK, and SHELBY, Circuit Judges.

PER CURIAM: Under the facts in this case it is not necessary to decide whether the provision for lead-bearing ores in paragraph 181, tariff act of 1897, is exclusive. On the merits the Board of General Appraisers and the circuit court ruled correctly.

The judgment of the circuit court is affirmed.

(T. D. 29552). Drawback on pig iron manufactured from iron ore, and steel billets, blooms, ingots, bars, structural material, guns, machinery, etc., manufactured from pig iron produced from imported iron ore and imported ferromanganese and ferrosilicon by the Bethlehem Steel Company, of Bethlehem, Pa.—T. D. 29365 of November 25, 1908, revoked.

TREASURY DEPARTMENT, *February 10, 1909.*

SIR: On the exportation of pig iron manufactured from imported iron ore, and steel ingots, blooms, billets, bars, rails, plates, structural material, castings, forgings, guns, gun mountings, projectiles, or machinery manufactured from pig iron produced from imported iron ore and imported ferromanganese and ferrosilicon by the Bethlehem Steel Company, of South Bethlehem, Pa., by the basic open-hearth process, a drawback will be allowed equal in amount to the duty paid on the imported materials consumed, less the legal deduction of 1 per cent.

The peliminary entry must show the marks and numbers of the shipping packages and the quantity and weight of each kind of product contained in each package and in the entire shipment.

The drawback entry shall show the quantity of each kind of exported article or material and the quantity of imported iron ore used in the manufacure thereof on which drawback is claimed. There shall be filed with each entry and made a part thereof a sworn abstract from the special manufacturing record hereinafter provided for. Said entry must further show, in addition to the usual averments, that the exported products were manufactured of the material and in the manner set forth in the manufacturers' sworn statement, dated December, 2, 1908, transmitted herewith for filing in your office.

A special manufacturing record shall be kept showing the quantity of pig iron manufactured, the quantity of imported ore used in the manufacture thereof, the analysis of and weight of metallic iron contained in each kind of ore used, the total quantity of metallic iron contained in the ores used and the average analysis thereof, the quantities of steel products manufactured, the quantities of pig iron produced from imported iron ore used in the manufacture thereof, and the quantities of imported ferromanganese and ferrosilicon used.

In liquidation, the quantity of imported iron ore which may be taken as the basis for allowance of drawback may equal that shown in the entry and abstract of the manufacturing record, after official verification of exported quantities, provided it shall not exceed 1.8 tons of imported ore for each ton of pig iron exported or used in the manufacture of steel products. The maximum quantity of pig iron produced from imported ore which may be taken as the basis for allowance of drawback on the steel products shall not exceed 1.0595 tons for each ton of steel products. The figures stated above are based on ore having the average metallic contents of 55.55 per cent. If the metallic contents of the ore is in excess of this percentage, the quantity of ore allowed for each ton of pig iron would be reduced accordingly.

The quantities of imported ferromanganese and ferrosilicon allowed for each ton of steel products exported shall not exceed 0.0082 of a ton of ferromanganese and 0.004 of a ton of ferrosilicon.

T. D. 29365 of November 25, 1908, providing for the allowance of drawback on steel products manufactured by the Bethlehem Steel Company, is hereby revoked.

Respectfully,

JAMES B. REYNOLDS,

(58807). *Assistant Secretary.*

Collector of Customs, Philadelphia, Pa.

(T. D. 1463). *Denatured Alcohol.*—Authorizing Formula 1 for use in the cleansing of filled gelatin capsules.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., February 16, 1909.

SIR: You are informed that Formula 1 (to 100 gallons of alcohol add 5 gallons of approved wood alcohol) is hereby authorized for use in the cleansing of filled gelatin capsules.

You will please inform ———, Brooklyn, N. Y., of this authorization, in compliance with their application of the 6th instant.

Respectfully,

JOHN G. CAPERS,
Commissioner.

Mr. E. B. JORDAN, *Collector First District*, Brooklyn, N. Y.

(T. D. 29563).—*Zinc Ores—Calamine.*—Decision of the United States circuit court of appeals, fifth circuit (suit 1961), United States *v.* Brewster (T. D. 29547), acquiesced in

TREASURY DEPARTMENT, *February 20, 1909.*

SIR: The Department is in receipt of a letter from the Attorney-General, in which he states that no steps will be taken looking to a review of the decision of the United States circuit court of appeals for the fifth circuit in suit 1961, United States *v.* Brewster (T. D. 29547), involving the classification of zinc ore known as carbonate, silicate, and sulphide of zinc.

The carbonates and sulphides were assessed with duty under paragraph 183 of the tariff act as crude metallic mineral substances, and the court affirms the decision of the Board and circuit court that the carbonates are free of duty under paragraph 514 as "calamine" and the sulphides are free of duty as minerals crude under paragraph 14.

You are therefore, hereby authorized to forward a certified statement for the refund of the duties collected in excess in this case.

While the circuit court of appeals affirms the decision of the Board and circuit court that the ores are free of duty, it sustained your assessment of duty under paragraph 181 upon the lead contents without regard to the percentage of lead contained therein, and you are hereby instructed to assess duty upon the actual lead contents in future importations of such ores.

Respectfully,

JAMES B. REYNOLDS,
(23706). *Assistant Secretary.*

Collector of Customs, Corpus Christi, Tex.

(T. D. 29601).—*Chemical Flasks.*—EIMER *v.* UNITED STATES.—U. S. circuit court of appeals, second circuit. February 16, 1909. No. 138 (suit 4963).

1. CHEMICAL FLASKS—BLOWN GLASSWARE—"BOTTLES."

"Thin blown-glass flasks designed for use in chemical laboratories are dutiable under paragraph 100, tariff act of 1897, as 'blown glassware,' rather than under paragraph 99 as 'bottles.'

2. STATUTORY CONSTRUCTION—HISTORY OF LEGISLATION.

"The bottle paragraph (No. 88) of the tariff act of 1894 contained a provision for 'bottle glassware' which was held to cover bottle-shaped receptacles, such as blown-glass chemical flasks, but which was omitted from the tariff act of 1897, while a provision (par. 100) for 'blown glassware' was inserted in the latter act. *Held* that it was intended that blown-glass flasks should no longer be grouped with bottles, but should be included in the larger group of 'blown glassware.'"

APPEAL from the circuit court of the United States for the southern district of New York.

(Decision in favor of the Government.)

The decision below (T. D. 29162) affirmed, without written opinion, a decision by the Board of United States General Appraisers, Abstract 15582 (T. D. 28223), which had affirmed the assessment of duty by the collector of customs at the port of New York on importations of Eimer & Amend.

Walden & Webster (*Henry J. Webster* of counsel), for the importers.

D. Frank Lloyd, Assistant United States Attorney, for the United States.

Before LACOMBE, COXE, and WARD, Circuit Judges.

This cause comes here upon appeal from a decision of the circuit court, southern district of New York, affirming a decision of the Board of General Appraisers which sustained the action of the collector in classifying for duty certain importations under the tariff act of 1897.

LACOMBE, *Circuit Judge:* The articles imported are chemical glassware, consisting of thin blown-glass vessels, such as Joliet's flasks, CO_2 flasks, etc., designed for use in chemical laboratories. The collector classified them for duty under

"PAR. 100. Glass bottles, decanters, or other vessels or articles of glass, cut, engraved, painted, colored, stained, silvered, gilded, etched, frosted, printed in any manner or otherwise ornamented, decorated, or ground (except such grinding as is necessary for fitting stoppers), and any articles of which such glass is the component material of chief value, and porcelain, opal and other blown glassware; all of the foregoing, filled or unfilled, and whether their contents be dutiable or free, sixty per centum ad valorem."

The importer contends that they should be classified under

PAR. 99. Plain green or colored, molded or pressed, and flint, lime, or lead glass bottles, vials, jars and covered or uncovered demijohns and carboys, any of the foregoing, filled or unfilled, not otherwise specifically provided for, and whether their contents be dutiable or free (except such as contain merchandise subject to an ad valorem rate of duty, or to a rate of duty based in whole or in part upon the value thereof, which shall be dutiable at the rate applicable to their contents) shall pay duty as follows: If holding more than one pint, one cent per pound; if holding not more than one pint, and not less than one-fourth of a pint, one and one-half cents per pound; if holding less than one-fourth of a pint, fifty cents per gross: *Provided*, That none of the above articles shall pay a less rate of duty than forty per centum ad valorem."

The articles are in fact blown glassware. The importers put in some evidence, which is vague and unpersuasive, to the effect that they were blown in a mold. We do not decide this case, however, on any insufficiency of proof; if it were conclusively shown that each one of these variously shaped flasks had been blown in a mold, it would not follow that they were "bottles, vials, jars, demijohns or carboys" and thus entitled to classification under paragraph 99. The word "bottle" has a tariff meaning which does not include these articles. "Chemical glassware" was provided for *eo nomine* in the tariff act of 1883, paragraph 143, and in the tariff act of 1890, paragraph 107. In the act of 1894 there was no provision for chemical glassware, but paragraph 88 provided not only for glass bottles, but also for "molded or pressed green and colored and flint or lime *bottle glassware*." This last phrase is descriptive of the articles in question; they were held dutiable under

that paragraph in Eimer *v.* United States (99 Fed. Rep., 423), where the court said:

"The expression, 'bottle glassware,' is broader than glass bottles and seems to cover something different from mere bottles used as containers. These bottle-shaped receptacles come within that description and seem to be included by it."

In the act of 1894 there was no provision for blown glassware. In the present act "blown glassware" is included in paragraph 100, and the "molded * * * bottle glassware" of 1894 is omitted from the new section 99. It would seem to be the natural conclusion that Congress intended that these articles should no longer be grouped with "bottles," but should be included in the larger group, "other blown glassware."

The decision is affirmed.

(T. D. 29614–G. A. 6880). *Microscope Slides with Specimens.*—Microscope slides of glass, containing specimens that are of greater value than the glass, are not dutiable under paragraph 100, tariff act of 1897, relating to articles of glass, ground, etc., but under Section 6 as unenumerated manufactured articles.—G. A. 1394 (T. D. 12798) followed.

United States General Appraisers, New York, March 9, 1909.

In the matter of protests 312302, etc., of American Express Company against the assessment of duty by the collector of customs at the port of Boston.

Before Board 1 (SHARRETTS, MCCLELLAND, and CHAMBERLAIN, General Appraisers; MCCLELLAND, G. A., absent).

SHARRETTS, *General Appraiser:* The merchandise in question is microscope slides composed of strips of glass 3 inches in length by 1 inch in width, with beveled edges and with a slight concavity in the center of each piece, in which concavity a microscopical subject—in the present case either physiological, botanical, or zoological—is mounted, a thin, flat, circular piece of glass being cemented to the edges of the concavity in the strip of glass to preserve the specimen enclosed therein. Duty was assessed on the disputed articles at the rate of 60 per cent. ad valorem under paragraph 100, tariff act of 1897, the importers alternatively claiming the same to be properly dutiable at the rate of 20 per cent. ad valorem as unenumerated manufactured articles under Section 6.

In G. A. 5794 (T. D. 25598) this Board held that pieces of crown glass identical with those used in the fabrication of the slides here in question were dutiable at 60 per cent. ad valorem under paragraph 100 as articles of glass ground. But in the case at bar the merchandise is not merely strips of ground glass. By reason of the fact that the specimens for microscopic investigation have to be prepared and mounted with consummate skill by scientific men the value of the microscopic slides is approximately eighteen times greater than that of the mere ground glass strips, and we so find.

An issue absolutely identical with that now before us was passed upon by the Board in G. A. 1394 (T. D. 12798), wherein it was held that the specimen was the essential feature of the article and that the glass was merely incidental to the display and protection thereof.

Based on our finding and following G. A. 1394 (*supra*), we sustain the protests and reverse the decision of the collector in each case.

(T. D. 29617–G. A. 6883). *Zinc Ores.*—Zinc ores—Calamine—Crude minerals—Lead-bearing ores. The zinc ores in the form of carbonates, silicocarbonates, and sulphides or concentrates are free of duty under paragraphs 514 (calamine) and 614 (crude minerals), tariff act of 1897, except that when containing lead, the lead content is subject to duty under paragraph 181.—United States *v.* Brewster (T. D. 29547) followed.

United States General Appraisers, New York, March 9, 1909.

In the matter of protests 221325, etc., of Prime Western Spelter Company against the assessment of duty by the surveyor of customs at the port of Kansas City.

Before Board 2 (FISCHER, HOWELL, and DE VRIES, General Appraisers).

FISCHER, *General Appraiser:* These protests are against the assessment of duty on certain zinc ores imported from Mexico. The ores are in the form of (1) carbonates or silicocarbonates and (2) sulphides or concentrates. The importers concede that if lead is present in these ores the importations should pay duty on the lead content at 1.5 cents per pound under paragraph 181, tariff act of 1897. They contest, however, the assessment of a 20 per cent. duty on the value of the zinc content, claiming that it is error to classify said ores as "metallic mineral substances in a crude state" under paragraph 183 of said act. The carbonates of zinc are claimed free under paragraph 514 as "calamine," or under paragraph 614 as crude minerals not otherwise specially provided for. The sulphides, ores known as zinc-blende, are claimed free of duty under paragraph 614.

These ores of zinc are in a crude state. The carbonates have been crushed and hand-picked; the sulphides have been subjected to a crude process of concentration. The object of such processes is to discard useless and foreign matter from the ore. To concentrate, as that term is used in mining, is to "separate (ore or metal) from its containing rock or earth." What the Government endeavored to prove in these cases may be briefly summarized as follows: That the ores, having been either crushed and hand-picked, or concentrated, are excluded by reason thereof from the provisions of paragraph 614, having been advanced in value or condition by refining or grinding, or by other process of manufacture; that the provision for metallic mineral substances covers the said ores, and that the merchandise should be classified under paragraph 183 rather than under paragraph 614, because the provision in the former paragraph is more specific than the latter; and that paragraph 514, which provides for the free entry of "calamine," applies only to the hydrous silicate of zinc, and does not embrace ores in the form of carbonates or silicocarbonates of zinc.

The issues thus raised were passed upon by the Board in G. A. 6540 (T. D. 27891). The testimony in that case was voluminous and exhaustive. The Board held that the construction given to the phrase "metallic mineral substances" in the case of Hempstead *v.* Thomas (122 Fed. Rep., 538) precluded the application of that provision to zinc ores in which the zinc did not appear as a free metal;

that the removal of foreign matter from the ore did not operate so as to take such ore out of paragraph 614; and that the term "calamine" included both carbonates and silicates of zinc, and was not to be confined to the hydrous silicate of zinc. The last clause in that decision of the Board may be here cited:

"Our conclusion is that the carbonates and silicates of zinc are included within the meaning of the term calamine as used in paragraph 514, and that they are free of duty under said paragraph and also under paragraph 614, and that the sulphide of zinc is free under the paragraph last named as crude minerals, etc., subject, however, to the qualification that when lead is found in these ores duty shall be taken on the amount of lead contained therein as described in paragraph 181."

Rulings of the Board, following G. A. 6540 (*supra*), on precisely similar ores, were appealed by the Government, with the result that the Board was affirmed in the case of United States *v.* Brewster (T. D. 29547, affirming T. D. 29006). The Treasury Department has announced its acquiescence (T. D. 29563), and, in accordance with these authorities, we sustain the claim in these protests that the zinc ores are free of duty under paragraph 514 or 614 of the tariff. The surveyor's assessments are modified to conform herewith; and in his reliquidation of these entries, where the lead content has been determined by a wet assay, it is proper to allow 1.5 units to find the fire assay, upon which the lead duty should be predicated.

(T. D. 1468). *Violations of the Oleomargarine Law—Hartman and Hartman v. United States.*—The decision of the United States circuit court finding the defendants guilty and imposing a fine of $1,000 and sentence of imprisonment for six months affirmed. The evidence showed that plaintiffs were engaged in the business of manufacturing oleomargarine by mixing with the white tax-paid oleomargarine a coloring material, which gave the product the yellow shade of butter, for the purpose of selling or disposing of the same to other persons than those of their own family tables, and that they had packed this colored product in packages which had contained colored oleomargarine tax paid and had been emptied without destroying the stamps upon the empty packages. The evidence resulting from a search of the premises is competent, although the search warrant was irregular and illegal.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., March 2, 1909.

The appended decision of the United States circuit court of appeals for the sixth circuit in the case of Hartman and Hartman *v.* United States is published for the information of internal-revenue officers and others concerned.

JOHN G. CAPERS, *Commissioner.*

(T. D. 1469). *Denatured Alcohol.*—Authorizing formula for special denaturant for use in the manufacture of fulminate of mercury.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., March 5, 1909.

SIR: This office is in receipt of application, Form 581, and bond, Form 582, of the ——— of your district, for specially denatured alcohol to be used in the manufacture of fulminate of mercury, and the same are hereby approved.

The application of ——— for permission to use the following formula—to 100 gallons of ethyl alcohol add one-half gallon of pyridin bases—is approved, and its use in the manufacture of fulminate of mercury is hereby authorized. This formula will be listed as No. 6 *b*, and its use will be restricted to factories operating in connection with either a distillery or central denaturing bonded warehouse.

Respectfully,
JOHN G. CAPERS,
Commissioner.

MR. H. C. H. HEROLD,
Collector Fifth District, Newark, N. J.

(T. D. 29394). Nov. 28, 1908.—Decision in favor of the government. Cocoa-butterine-cocoanut oil, manufactured. A cocoanut oil which has been subjected to a process of manufacture and is sold to confectioners and bakers is held dutiable under paragraph 282, tariff act of 1897, as "cocoa-butterine" rather than under paragraph 626 as cocoanut oil.

(T. D. 29404). Dec. 12, 1908.—Drawback on incandescent gas mantels manufactured by the Solar Light Company, of New York City, with the use of imported thorium nitrate. T. D. 27043 of January 27, 1906, extended.

(T. D. 29431). Nov. 28, 1908. Decision partly adverse to the Government.

1. Orchil extract—Persian-berry extract—unenumerated articles—drugs. Orchil and Persian-berry extracts are not "drugs" within the meaning of paragraph 20, tariff act of 1897, but are dutiable as unenumerated manufactured articles under Section 6.

2. Orchil—orchil extract. Orchil extract is a manufactured article, and is therefore excluded from the provision in paragraph 628, tariff act of 1897, for "orchil, or orchil liquid."

(T. D. 1444). Dec. 16, 1908. Malt extracts, held out to be medicinal in character, may be shipped under trade name without violation of Section 3449, Revised Statutes.

(T. D. 29342.) Dec. 21, 1908. Distilled spirits not exported in good faith not entitled on return to United States to entry under Section 2500, Revised Statutes, nor to warehousing privileges.

(T. D. 29436—G. A. 6842). Dec. 23, 1908. A watermark in the form of a firm's name, business and address does not constitute a decoration, and writing paper so marked is not subject to the additional duty provided in paragraph 401, tariff act of 1897, for "writing * * * paper, * * * decorated in any manner."

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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EDITORIALS.

FIREPROOF MATERIALS.

RECENT developments indicate an approaching general awakening to the crying need for fireproof buildings and methods of construction. The lessons taught by the Baltimore, San Francisco and Chelsea fires have borne and are bearing fruit. Large buildings, office and factory buildings, in and near the larger cities—especially those that have suffered greatly by fire—are being designed and built with the most careful attention to the minimizing of fire risks. Materials of construction are receiving more attention and actual tests of their fire-resisting qualities are multiplying; and while the adherents of concrete and terra cotta tile are waxing warm in the discussion of their respective merits both these materials are finding a place in real fire-proof construction that cannot be seriously damaged by any ordinary conflagration.

We have brick, stone or concrete walls and reinforced concrete or tile-covered columns, floors and stairs, so that there is little combustible material in the average modern office building, but the furniture, and even this and the door- and window-frames and trimmings may be obtained in metal or other non-combustible material. With such fire-proof material at hand, even to doors, window-frames and sashes and flooring, and with fire-proof construction thoroughly tested and approved by competent authorities and by fire underwriters, it is a serious reflection on our intelligence as communities that we continue to build school-houses, theaters, hotels and other public buildings with wooden floors, partitions and stairs even when the outside walls (which is not always the case) are not themselves combustible.

But, as has already been intimated, capital is now awake and humanity is also slowly awakening to the necessity of protecting human life; of rendering impossible such calamities as the Collingwood school disaster and others equally familiar, and of making the wholesale destruction of property a thing of the past by the use of materials that will not burn. That such buildings can be built has been established beyond any doubt. The problem now is to so finish and furnish them that the possibility of fire and the amount of material on which it might feed shall be reduced to a minimum.

A test was recently made at the Columbia University fire-testing station of a fire-proof hollow block of a new material passing under the trade name of "Sagax," consisting of 60 per cent. ground straw with a magnesium cement as a binder. The material is said to be 25 per cent. lighter than terra cotta of the same size and strength and fully as fire-resisting, and it has had the added advantage that it may be cut, painted or nailed to like wood.

There is a large field for further experiment and exercise of inventive genius in the improvement of and addition to the fire-proof materials and processes now in use.

The relation of the industrial chemist to the problems involved is self-evident; it is chiefly to him that the world is indebted for all that has thus far been achieved, and it is to him that the world looks for the improvements that are bound to come,

—satisfactory substitutes for wood and efficient methods for fire-proofing fabrics that must be used in furnishings as well as the improvement and cheapening of existing methods and materials of construction.

ERNEST B. McCREADY.

ORIGINAL PAPERS

THE MANUFACTURE OF CARBON ELECTRODES.

By G. A. ROUSH.

Received December 26, 1908.

The manufacture of carbon electrodes is each year becoming a more important industry, as it must necessarily keep pace with the constantly increasing number of electrochemical processes, both electrolytic and electrothermic, in which electrodes of carbon or graphite are parts of the apparatus. The amount of carbon used as electrode material is increasing immensely every year. In 1900 the value of the furnace carbons reported for the United States Census, was approximately $11,000.[1] Now electrodes to that value are used every month in the smelting of aluminum alone. Large quantities are also used in the manufacture of caustic soda, calcium carbide, carbon disulfid, phosphorus, ferro-alloys, etc., and after graphitization by the Acheson process, in many other processes. The production of carbon electrodes of various sorts, for 1906, was probably in the neighborhood of 10,000,000 pounds, not including large quantities of battery carbons, for electrodes in dry and wet primary batteries.

The manufacture of electrodes for furnace work, of course, is simply an adaptation of the process for making arc light carbons. The dynamo and arc light not having been perfected until 1877–1880, the demand for carbon electrodes of all kinds was very limited, and all that were made before this time were for experimental purposes only, and were made by hand. With the introduction of the Brush dynamo and arc light, a demand was created and the supplying of carbons for these lamps then became a problem of importance.[2]

The development of the American carbon industry is largely due to Chas. F. Brush and W. H. Lawrence, of Cleveland, Ohio, and to them belongs the credit for the discovery of the fitness of petroleum coke as the basic raw material for the manufacture of carbons. The experiments then made to ascertain the grain best adapted for burning in the electric arc, and the most suitable adhesive material to bind the carbon particles together laid the basis of the industry which has continued to the present day, with such additions as experience has shown advisable and the invention of the automatic and labor-saving machinery has made possible.

The raw materials used in the manufacture of carbon electrodes for electrochemical and electrometallurgical work are:

1. Coke.
2. Hard pitch.
3. Soft pitch.
4. Tar.
5. Oil.

These materials will be taken up and discussed in the order named.

Coke.—For some purposes where a relatively high amount of ash is not objectionable, a seventy-two hour Connelsville coke or a calcined anthracite coal might be used. These make a very hard, dense carbon, but their high ash content prohibits use in all electrolytic processes where the ash freed by the disintegration and consumption of the carbon would contaminate the electrolytic bath.

Methods have been devised for purifying such materials by the removal of the ash[1] but so far as is known none of these are in commercial use.

For these reasons except in special cases, the material used is petroleum coke—the residue left in the still in the refining of crude oil. After calcining to remove volatile matter this gives a hard, dense material, low in ash, admirably suited for the purpose. For the manufacture of electrodes a coke from sulphur-bearing oil is generally used, since it is considerably cheaper than coke from a non-sulphur-bearing oil, and the presence of the sulphur in the electrodes is not objectionable as it is in the case of lighting carbons.

The coke as purchased contains 6–10 per cent., and sometimes as high as 14 per cent. of volatile matter which must be removed by calcination before the coke can be used. If the volatile matter

[1] Twelfth Census Report of the U. S., Vol. 10, p. 70.

[2] A fairly good historical account of the development of the manufacture of carbons can be had from "The Manufacture of Carbons for Electric Lighting and Other Purposes," by Francis Jehl, pp. 3–17 (The Electrician Printing and Publishing Co., London), and the Twelfth Census Report, Vol. 10, p. 170 1

[1] Process for removing silica from coke, U. S. P. 733,389, July 14, 1903; C. M. Hall, abstracted in *Electrochem Industry*, Vol. 1, p. 467 (1903). Method of purifying electric lighting carbons, U. S. P. 542, 982, July 23, 1895. "The Manufacture of Carbons for Electric Lighting and Other Purposes," Jehl, pp. 87–93.

is over 10 per cent., the coke cakes together in the calcining retorts, and is very difficult to remove. The coke usually carries 0.02–0.06 per cent. of ash.

The raw coke costs about $12.00 per ton including the freight, from the refineries at Philadelphia, and Bayonne, N. J., to West Virginia.

In some cases, to impart better mechanical wearing properties to the material, a small portion of the coke is replaced by lampblack.

Pitch.—The coke forms the main body of the electrode. The material next in importance is the binder which is used to hold the coke particles together For this purpose coal tar pitch is mainly used. Both hard and soft pitch are used, either singly or together, depending on the fineness of the coke and the kind of electrode being made.

The hard pitch should soften at 160–170° F., and contain 40–45 per cent. of residue insoluble in benzol. It usually carries about 0.10 per cent. of ash, mostly oxid of iron.

The soft pitch is soft enough at ordinary temperatures to be easily dented with the finger nail.

The cost of the pitch is about $10.00 per ton.

Tar.—For the sake of special properties in the electrode, to be discussed later, a part of the pitch is sometimes replaced by coal tar.

Oil.—A small quantity of summer oil, the last distillate in the refining of crude oil, is used simply as a lubricant.

The process of manufacture may be divided as follows: (1) calcining, (2) milling, (3) mixing, (4) plugging, (5) forcing, (6) baking, (7) cleaning and sorting, (8) testing.

Calcining.—As has been said, the coke, when received, contains a considerable percentage of volatile matter, which, to avoid a large and uneven shrinkage in the baking, must be removed before the coke can be used.

The raw coke is crushed to about three-fourths inch size in an ordinary gyratory crusher, and is elevated to a storage bin over the calcining retorts, into which it is fed by gravity. The retorts consist of circular pockets of fire-brick, so arranged that the fire plays all around them. Figs. 1 and 2[1] show diagrammatic sections of a retort. The retort is charged at B and discharged at D by means of gate valves.

The calcined coke is discharged into wheelbarrows and spread out on the floor to cool, when it is shoveled into screw conveyers and carried to the milling department.

The coke as it comes from the retorts should contain less than 0.2 per cent. of volatile matter; a higher percentage than this calls for re-calcining. The ordinary run of coke can be reduced to this point in forty-eight hours, but a coke running extra high in volatile matter may require more time.

Counting fuel, labor, loss in weight, etc., it costs approximately $5.00 a ton to calcine the coke.

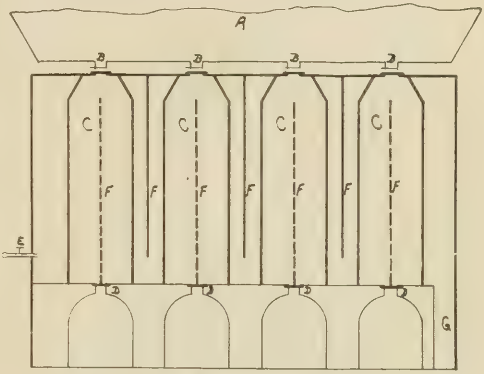


Fig. 1.—Coke retorts.

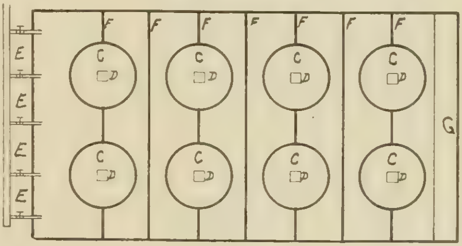


Fig. 2.

A, Coke bin.
B, Gate valve for charging.
C, Retort.
D, Gate valve for discharging.
E, Gas valves.
F, Flue walls.
G, Flue to stack.

Milling.—The calcined coke is very porous and in order to make a compact carbon, must be reduced to a flour. Varying degrees of fineness are used for different sizes of carbons, the coarser flour being used for the larger sizes, and the finer for the smaller sizes.

A hard, dense carbon is at all times most desirable, and the finer the flour, the lower the porosity of the carbon made from it, but in the larger sizes, low porosity is sacrificed to a certain extent, since

[1] All the illustrations accompanying this article are merely diagrammatic, and are not intended to adhere strictly to proportions or show details and dimensions.

a somewhat coarser flour lessens the liability of the carbon to crack across the end in baking. Following are three typical analyses of the flours used in the various sizes:

	For small sizes, per cent.	Medium sizes per cent.	Large sizes, per cent.
On 100 mesh..........	0.8	5.0	10.0
On 140 mesh..........	7.7	17.3	20.5
On 200 mesh..........	27.5	21.7	19.0
Through 200 mesh.....	64.0	56.0	50.5

The finest flour is produced most satisfactorily in the Raymond impact pulverizer, shown in Fig. 3. In this mill the material is ground against the inside of a heavy ring, F, by a wheel, E, suspended

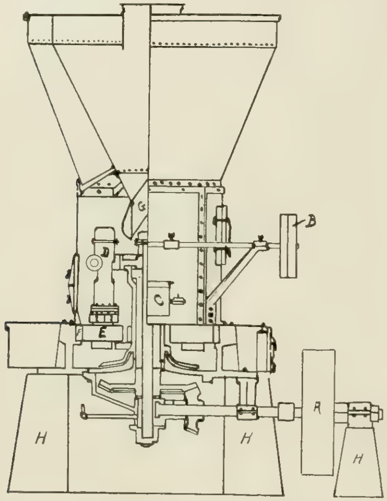


Fig. 3.—Raymond impact pulverizer.

A, Drive pulley; B, Feed drive; C, Feed box; D, Swinging arm, E, Revolving impact wheel; F, Impact ring; G, Cone and chute for returning coarse material for regrinding; H, Concrete foundation.

at the end of a rotating arm D, the wheel being forced against the ring by the centrifugal force of the rotation. The crushed material, falling through to the bottom of the mill, is elevated by a stream of air from a fan. The coarser particles, of course, require a heavier blast of air to raise them than the fine material, and thus, by regulating the speed of the fan, the fineness of the material can be controlled, the coarser matter being allowed to drop back and be crushed again.

With this mill, it is a simple matter to get material of such a fineness that 98 per cent. will pass a 100-mesh sieve, and 92 per cent. will pass a 200-mesh sieve, without the expensive operation of bolting.

The current of air carrying the pulverized material is passed through a settling chamber where all but the finest dust settles out. The air from the settling chamber goes through a dust collector where it is filtered through muslin, and the last of the dust removed and returned to the settling chamber.

If for any special purpose, an exceptionally fine flour is desired, the fines from the dust collector may be saved separate, giving a material too fine to classify by sifting, 100 per cent. passing through a 200-mesh sieve.

The coarse flours are produced either in the Raymond mill with a higher speed on the fan, or in the ordinary Buhr mill with or without bolting, according to the fineness desired. Only the coarsest flour can be used from the Buhr mill without bolting.

The bolters used for this purpose are the same type as ordinarily used in flour mills.

The hard pitch is crushed to approximately one-half inch size in a gyratory crusher, and the soft pitch is melted in a steam jacketed kettle.

The various grades of flour and the hard pitch are stored in bins directly over the mixing room. The soft pitch and the supply of summer oil should be in the mixing room.

Mixing.—It may be stated as a general rule that the hardness of a carbon increases with the fineness of the flour and the increasing fluidity of the binder used in it. By properly controlling these conditions, carbons of different hardness may be produced according to requirements. This rule, however, cannot be worked at pleasure since the nature of the substance in hand sometimes prohibits. For exceedingly fine flours, soft pitch or tar or a mixture of the two must be used, since it is very difficult to coat the very fine particles with a binder of such a high melting point, and low degree of fluidity as the hard pitch.

The finer flours require more pitch to bind them together than do the coarser ones. The amount also varies with the melting point of the pitch and the size of the carbon to be made, a small carbon requiring a softer composition than a large one. With an ordinary grade of hard pitch it will require 30-40 per cent. of the weight of the coke. For the ordinary medium grade of electrode, hard pitch is used almost entirely.

Following is given the composition of some of the more common "mixes:"

(1) For ordinary electrodes.

Coke, 325 pounds.

Hard pitch, 110 pounds.
Oil, 1 gal.

(2) For a somewhat finer flour or a pitch of a higher melting point.

Coke, 325 pounds.
Hard pitch, 115 pounds.
Oil, 2 gal.

(3) For a coarse flour.

Coke, 325 pounds.
Hard pitch, 40 pounds.
Soft pitch, 4 gal.
Oil, 1 gal.

(4) For a carbon to stand heat and wear but not used as electrode.

Coke, 325 pounds.
Lampblack, 20 pounds.
Hard pitch, 30 pounds.
Tar, 10 gal.

A variation of two pounds of pitch in a batch can be detected in forcing the carbon by one experienced in handling it.

The materials weighed out in the proper proportions are run into steam-jacketed mixing kettles (Fig. 4) with revolving blades and mixed for about twenty minutes. The mix comes from the kettles as a very stiff dough, every particle of coke being covered with a thin coating of melted pitch. The mixing must be sufficient to insure a uniform product, or unequal shrinkage and cracks will result on baking. The hot mix has a temperature of 265–275° F.

Plugging.—The hot mix from the mixing kettles is shoveled into heavy cast iron hoops, and by means of hydraulic presses,[1] pressed into cheeses about six inches thick, and the same diameter as the opening in the press in which the carbons are to be formed. This may vary from four to twenty four inches, depending on the size of the carbons to be made.

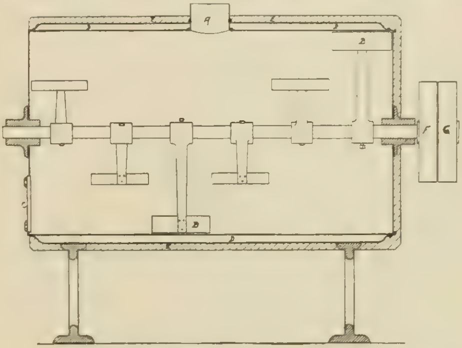


Fig. 4.—Mixer with one-half of casing removed.
A, Charging aperture; B, Mixing paddles; C, Discharge door; D; Steam jacket. E, Magnesia covering. F, Drive pulley; G, Idle pulley.

The plugging puts the mix into a compact form easily handled, and presses out most of the air, thus avoiding the presence of large air bubbles in the carbon.

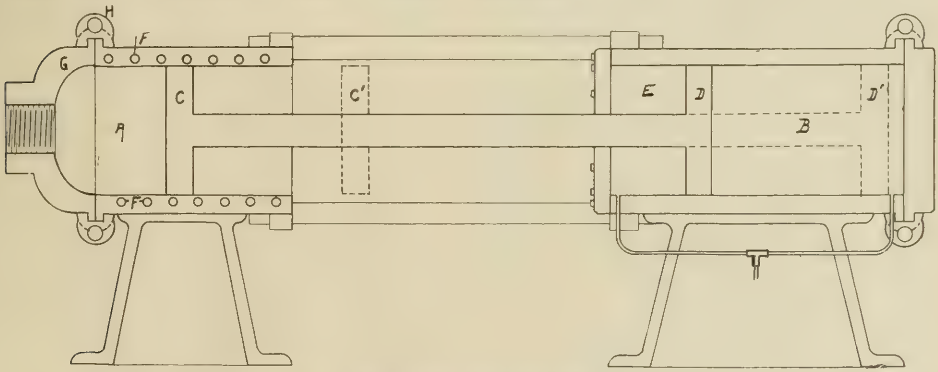


Fig. 5.—Carbon press, sectional view.
A, Carbon end; B, Water end; C, Carbon ram; D, Water ram; E, Reverse water space; F, Steam coil; G, Die head; H, Collar; C′ and D′ show the positions of C and D when charging.

Forcing.—These cheeses, or "plugs," are then forced by hydraulic pressure through a die the size

[1] An illustration showing the style of press used for this work may be found in *Electrochem. Industry*, Vol. 1, p. 51 (1902).

and shape to make the carbons of the desired cross section, various sizes of round and square dies being kept in stock.

The press for the forcing, generally known as a "Jumbo," is shown in cross section in Fig. 5. A is the carbon end of the press, B the water end; C is the carbon ram and D the water ram. E is the reverse water space, for withdrawing, C for recharging C′ and D′ show the position of C and D when recharging. F is a steam coil in the jacket of the carbon end to keep it the same temperature as the carbon it contains. The head G, carrying the desired die in the threaded opening, is held in place by the collar H, bolted above and below.

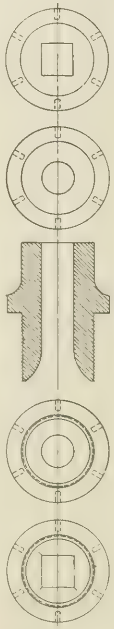
Although it is often made smaller, to secure the best results the diameter of the water ram should be at least equal to the diameter of the carbon ram. Otherwise it is sometimes difficult to get sufficient pressure for forcing a stiff mix, or a charge that has accidentally been left to cool too long.

Dies for all sizes in common use are kept in stock. Fig. 6 shows a solid die for round or square carbons. A die of this kind is, of course, of a fixed size, and a separate die must be had for each size of carbon made. Fig. 7 shows an adjustable die for rectangular carbons. By supplying extra side plates, D, of varying width and thickness, rectangular carbons of any size up to the extreme limit of the die may be made. Carbons of irregular outline require a separate die for each shape and size.

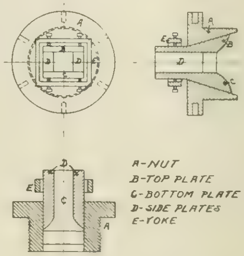
When the carbon is released from pressure on emerging from the die, it expands considerably in size, in smaller sizes, as much as four or five per cent. This increase in size, however, is more than counteracted by the shrinkage in baking, so the opening in the die must be larger than the finished carbon is to be. Since the expansion of the green carbon and shrinkage in baking both depend on so many different factors—size of flour, composition of mix, melting point of the pitch, temperature of forcing, pressure of forcing, size of the carbon, etc.—it is impossible to give any definite figures as to the relative sizes of the die and the finished carbon. This must be more or less a matter of "cut and try." The diameter of the die is usually about 3–5 per cent. greater than the diameter of the desired carbon.

The plugs fresh from the plug presses are usually too soft to work well in the jumbo, and must be allowed to cool for a time. If run too hot, the pressure required to force the mix through the die is not sufficient to press the separate plugs into one coherent mass. The plugs entering the jumbo vary in temperature from 200–240° F., according to the composition of the mix, the size of the plugs, and the size of the carbons to be made.

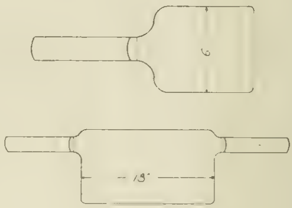
The jacket of the jumbo should be kept at a temperature about 5–10° higher than the plugs, to prevent the formation of a hard shell around the outside of the mass of carbon.



SOLID DIE.
ROUND OR SQUARE
FIG. 6



ABUSTABLE SQUARE DIE FIG 7



CUTTING KNIVES.
FIG 8

The pressure required for the forcing varies with the temperature and composition of the mix, and the relative size of the plugs and the die through which they are to be forced, generally ranging from 1000 to 3000 pounds per square inch. If too high a pressure is used, the carbon expands so rapidly and so much on emerging from the die as to cause it to split radially from end to end.

The carbon as it comes from the die is caught in wooden or iron forms, and while still warm and plastic, is cut to the proper length by hand with heavy knives (Fig. 8) and left in the forms to cool and harden. After hardening so they can be handled without losing their shape, they are loaded

into trays and carried into the furnace room on trucks.

A large percentage of the mix is lost in the forcing, as scrap, consisting of spoiled and defective carbons, trimmings, etc. This frequently amounts to 25 per cent. of the mix handled. A portion of this scrap is used in the furnace room, as will be explained later; the remainder, after cooling and hardening, is crushed to a flour and mixed again as a part of a new batch, correction being made for pitch it contains.

Baking.—The green carbons, being composed argely of pitch, are nonconductors of electricity and require baking to render them conducting. This removes the volatile portions of the pitch, and leaves the particles of coke-flour bound together by the coke thus formed. The carbons must be protected from the action of the air while being baked, and this is done by burying them in the furnace in fine sand.

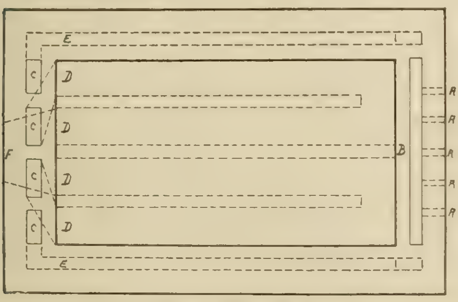


Fig. 9.—Baking furnace, top view.

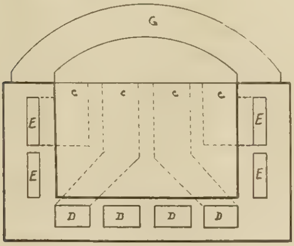


Fig. 10.—Cross section.

A, Opening for gas burners; B, Distributing wall for gas; C, Distributing flues; D, Flues in bottom of fce.; E, Flues in sides of fce.; F, Flue to stack; G, Fce. top.

Figs. 9 and 10 show the construction of the baking furnaces. Flues are so arranged in the walls and bottom that the space inside the furnace is completely surrounded by fire. The inside dimensions of a furnace such as shown, are $12'8'' \times 7' \times 3'$. The furnaces are gas-fired.

Patents have been granted[1] for an electric furnace for baking electrodes, but from the best information at hand, it is believed that the process was never in commercial use.

In filling a furnace the bottom is covered with a layer of sand; on this is placed a layer of carbons, care being taken that they do not touch each other, the space between being filled with sand. Over this is placed another layer of sand, then another of carbons, and so on until the furnace is full. If there is not sufficient space between the carbons, the volatile matter boiled out of the pitch will cake the sand together around them. This space varies from one-eighth inch or less for carbons one inch in diameter, to two or three inches for a twelve-inch carbon. The top layer of sand is three or four inches thick, and is covered with brick or tile, forming the seal of the furnace.

Great care must be taken that the layers of sand on which the carbons are packed are perfectly smooth and level, and that the sand is packed firmly around them at every point. In firing the furnace when the melting point of the pitch is reached, the carbon becomes very soft and plastic and will assume any shape allowed by the sand in which it is packed. A small leak in the floor of the furnace allowing the sand to trickle through into the flues during the firing is liable to cause crooks and cracks in all the carbons immediately above it.

After the fire is turned out and the furnace begins to cool off, enough air usually enters through the seal of the furnace to considerably damage the top layer of carbon by oxidation. For this reason the top layer is usually green carbon scrap, brought from the furnace room for this purpose, which after baking is ground up and used in making battery carbons.

The number of carbons packed in a furnace depends entirely on their size. The following table gives the number that will pack in a furnace, for some of the common sizes:

$1\frac{1}{4} \times 15$ inches[2]	10900
$\frac{7}{8} \times 2 \times 30$ inches	3600
$1\frac{3}{4} \times 3 \times 36$ inches	1408
$3\frac{3}{8} \times 18$ inches	1396
$4 \times 4 \times 13\frac{1}{2}$ inches	1086
$5\frac{1}{4} \times 19\frac{1}{2}$ inches	564

[1] U. S. P. 705,076, July 22, 1902; C. M. Hall, abstracted in *Electrochem. Industry*, Vol. 1, p. 30 (1902) and Vol. 2, p. 7 (1904).

[2] Where only two dimensions are given, the carbon is round, the smaller being the diameter.

4 × 30 inches	470
4 × $8\frac{3}{4}$ × 15 inches	305
12 × $49\frac{1}{4}$ inches	10
12 × 12 × 50 inches	10
12 × 60 inches	5

With the smaller sizes the number varies somewhat according to the size of the scrap packed on top of the furnace. With the larger sizes, more could be packed were it not for certain rules that are followed in packing. Whenever possible carbons are packed with the long way of the carbon running the long way of the furnace, and if rectangular in shape, with the narrow edge up. As can be seen from the construction of the furnace, most of the heat is received from the top, bottom and sides, rather than from the ends. This method of packing permits the heat to pass through the carbon, through its shorter dimensions, so that, as near as possible, all parts of a single carbon are at the same temperature at the same time, thus giving less liability of uneven shrinkage, which causes warping and cracking.

The proper firing of a furnace requires considerable experience. At its best this operation requires such a large amount of time and fuel, that it must be accomplished with as great an economy of both as possible. Yet just as great care must be taken not to force a furnace too fast, or its entire contents may be ruined. If the pitch in the green carbon is volatilized faster than the gas can escape through the pores of the carbon, it will cause bubbles in the carbon and uneven shrinkage with its attendant warping and cracks. The firing throughout must be steady and even, and must be judged from the appearance of the fire, the amount of pitch gas escaping through the seal, and the temperature measured in a test pipe leading through the walls about two feet into the contents of the furnace. A furnace of small goods can be fired faster than one of heavy goods.

A furnace begins to "gas" after three or four days' firing; seven to seven and a half days should see the gassing practically over. The total firing requires ten to fourteen days according to the size of the material and the rapidity with which it can be forced. Figs. 11 and 12 show the temperature curves of two furnaces, showing the rate of firing.

Most carbons are baked to a final temperature of 1020° C., although some need be taken only to 950°. Practically all electrodes are baked to 1020°, since the higher the temperature of baking, the higher the density and conductivity of the carbon. The carbon should have a resistance of 0.0016 ohm for a one-inch cube,[1] and have a safe carrying capacity of 25 amperes per square inch of cross section.

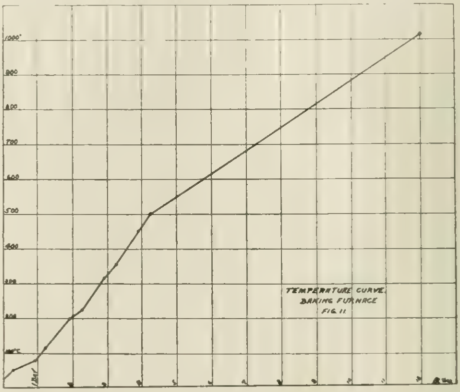


Fig. 11.

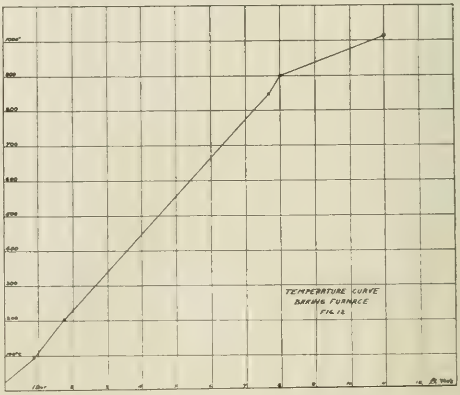


Fig. 12.

The density produced by various temperatures is given by Fitzgerald[2] as follows:

Temperature	Density.
Dull redness	1.9141
Above melting point of $CaCl_2$—below melting point of silver	1.9612
Above melting point of silver	1.9853
Above melting point of copper—below melting point of cast iron	2.0061
Above melting point of cast iron	2.0363
Heated in platinum crucible over blast lamp	2.0585

The variations in temperature in the various parts of the baking furnace were shown by the following experiments:

[1] "On Carbons for Electrometallurgy." Fitzgerald and Forssell. *Trans. Amer. Electrochem. Soc.*, **11**, 321 (1907).

[2] *Trans. Amer. Electrochem. Soc.*, **6**, 33 (1904), abstracted in *Electrochem. Industry*, **2**, 415 (1904).

1. Samples were tested for density from the center of each layer in a furnace containing nine layers, with the following results:

No. of layers (from top).	Density.
1	2.00
2	2.00
3	1.995
4	2.00
5	2.00
6	2.00
7	1.99
8	1.974
9	1.96

2. In another furnace samples were taken:

(1) From the end of the furnace next to the burners.

(2) In the middle of the furnace.

(3) From the end of the furnace next to the distributing flues (see Fig. 9).

Sample No.	Density.
1	2.026
2	2.005
3	2.018

The baking out of the pitch from the green carbon causes a considerable shrinkage in both weight and dimensions, varying somewhat with the composition of the mix, and the size of the carbon. The longer the dimension, the smaller the percentage of shrinkage. Rough figures on the shrinkage between green and baked carbons are given in the following table:

Approximate length of dimensions of inches.	Per cent. shrinkage.
1	5.5
2	4.9
3	4.0
4	3.4
6	3.2
12	2.3
24	2.2
48	2.0

Shrinkage in weight averages 13.4 per cent. loss.

The final temperature is judged by an alloy of gold and silver in such proportions that it melts at 1020° C. When the furnace reaches such a temperature that a small square of the alloy melts readily when placed in the test pipe, the fire is turned off and the furnace allowed to cool.

It requires four or five days for the furnace to cool sufficiently for it to be opened and the contents removed. If a furnace is opened too soon and its contents exposed to the air at too high a temperature, oxidation and cracking will result.

When the furnace is opened the sand is shoveled out, run through a small gyratory crusher, screened through a trommel screen and is then ready for use again.

Cleaning and Sorting.—The carbons are taken out of the furnace, and adhering sand removed by brushing with a wire brush. The cleaning is almost all done by hand, no very satisfactory machine for this purpose having been devised. A furnace of five 12 × 60 carbons or even one of ten 12 × 12 × 50's is not a particularly difficult proposition, but one containing eleven thousand 1 1/4 × 15's is another story.

While the carbons are being cleaned, all defective ones are thrown aside, leaving only the perfect ones, ready for shipment, if the laboratory tests on the lot are favorable.

The culls are either used for making battery carbons or may be ground up and the flour used the same as the regular coke flour. It however requires somewhat less pitch in mixing and makes a carbon that shrinks less in baking, and is slightly harder.

Testing. While the furnace is being emptied, samples are taken to give an average of the lot by chipping from carbons in all parts of the furnace, and taken to the laboratory for examination. The tests made include apparent density, real density, and ash.[1]

The apparatus for the density determinations consists of a volumeter tube[2] graduated to 100 cc. in divisions of 0.2 cc. fitted with a rubber stopper, through which passes a glass tube connected to a vacuum pump.

For ordinary carbon, it has been found that the size of the pieces in the sample has no effect on the results, and in general, there is no practical difference between the center and outside of an electrode. The essential thing is to see that there is no sand adhering to the sample. Temperature does not affect the results, and the pressure need be reduced only to two inches of vacuum. These conditions give results checking to hundredths.

Apparent Density.—The sample—30 grams or more—is weighed and given a coating of shellac by covering it for a few minutes with a light solution of a good grade of shellac in wood alcohol, and drying. The tube is carefully filled to about 50-60 cc. with water free from air bubbles. Read the tube, and introduce the sample, using care not to spatter the sides of the tube. Jar the tube slightly to remove adhering air bubbles, and read again. The difference between the two readings,

[1] "Testing Carbon Electrodes." Fitzgerald, *Trans. Amer. Electrochem. Soc.*, Vol. 2, p. abstracted in *Electrochem. Industry*, **1**, 68 (1902).

[2] Eimer and Amend Catalog, No. 7179, p. 395 (1905).

divided into the weight of the sample, gives the apparent density.

Real Density.—For the real density instead of water, use coal oil of 0.78 sp. gr. If new, exhaust in a vacuum for fifteen minutes. Fill the tube to 50–60 cc., allow to stand a few minutes and read. Introduce the weighed sample—30 grams or more—and apply the exhaust gradually. After most of the bubbling has ceased, it can be increased to the limit, and the tube jarred slightly to help free any bubbles. Care must be taken that no oil escapes through the connecting tube to the pump. The action is complete in 6–10 minutes. Remove the exhaust, allow to stand a few minutes and read again. The difference between the two readings, divided into the weight of the sample, gives the real density.

For ordinary, or purely comparative results this method is sufficient, but where greater accuracy is desired, the pycnometer method should be used. The pycnometer is weighed empty, full of water, and full of oil, the bottle being filled each time to 25° C. in a thermostat. The weight of the oil divided by the weight of the water, multiplied by the factor of contraction, to convert water at 25° to water at 4°, gives the density of the oil.

A sample of about 30 grams of carbon is ground to 100-mesh; ten grams of this are weighed into the pycnometer which is then filled half full of oil and exhausted under a bell jar, or in a vacuum desiccator until all bubbles cease. Then more oil is added and further exhaustion continued. Finally the bottle is completely filled and placed in the thermostat till it comes to 25° C., and is then dried and weighed.

The calculation for the density of the carbon is as follows:

D = density of carbon.
d = density of oil.
W = weight of sample in grams.
b = weight of pycnometer.
O = weight of oil in pycnometer containing no sample.
O′ = weight of oil in pycnometer containing the sample.
0.0012 = density of air.
0.997071 = factor of contraction of water from 25° C. to 4° C.

$$\text{Then D} = \left(\frac{W}{(W+b+O) - (W+b+O')} \times d\right) + 0.0012.$$

This method gives results which average 0.025 higher than the volumeter method.

Ash.—Five grams of the sample are burned in a muffle in a porcelain crucible, and weighed.

$$\frac{\text{Wt. ash} \times 100}{5} = \text{per cent ash.}$$

With ordinary electrodes, the apparent density varies from 1.55 to 1.70; the real density from 1.95 to 2.05; and the ash, from 0.10 to 0.30 per cent.

As can be seen from the apparent density, carbons will approximate 100 pounds per cubic foot in weight.

Carbons for Graphitization.—A large percentage of the electrodes used in the various electrochemical processes are of graphite. Acheson's process of converting amorphous carbon into graphite[1] makes possible the conversion of formed carbon electrodes into graphite. It is not necessary to describe this process here, since it can readily be found in the literature.[2] We shall consider only the production of the electrodes of amorphous carbon ready for graphitization. This is just the same as the production of ordinary electrodes except the composition of the mix, which is as follows:

Coke	325 pounds
Hard pitch	103 pounds
Soft pitch	½ gal.
Oil	1 gal.
Oxid of iron	5 pounds

According to Danneel,[3] aluminum oxid is more suitable for this purpose than iron oxid, but iron oxid is the one that is used. The presence of some metal in the carbon is necessary, since the conversion into graphite depends on the formation of a metallic carbide, and its subsequent decomposition by a higher temperature, volatilizing the metal, and leaving the carbon in the form of graphite.

All scrap and culls, both green and baked, must be worked back into the process, since carbon containing iron cannot be used for battery purposes.

The finished carbon for graphitization should have an ash content of approximately 1.5 per cent., and a real density of 2.00. A density below this point calls for the re-baking of the material, at a heavy cost for labor, time and fuel.

Some idea of the possibilities of growth in the

[1] U. S. P. 542,982, July 13, 1895, abst. in *Electrochem. Industry*, **3**, 416 and 482 (1905); U. S. P. 568,323, Sept. 29, 1896, abst. in *Electrochem Industry*, **3**, 482 (1905); U. S. P. 617,979, Jan. 17, 1899, abst. in *Electrochem. Industry*, **3**, 417 (1905) and **4**, 42 (1906); U. S. P. 645,285, March 13, 1900, abst. in *Electrochem. Industry*, **3**, 416 (1905) and **4**, 42 (1906); U. S. P. 702,758, June 17, 1902, abst. in *Electrochem. Industry*, **3**, 417 (1905) and **4**, 42 (1906), U. S. P. 711,031, Oct. 14, 1902, abst. in *Electrochem Industry*, **1**, 130 (1902) and **3**, 417 (1905).

[2] *Electrochem Industry*, **1**, 52 (1902) and **3**, 417 (1905), and above patents, note (1).

[3] *Zeit. Elektrochemie*, Sept. 25, 1902, abst *Electrochem Industry*, **1**, 106 (1902).

carbon industry can be had from the patent statistics. During the year 1907, over eighty patents were granted on processes or apparatus using carbon or graphite as electrodes—about 40 per cent. of the total electrochemical patents granted, exclusive of battery patents.

THE DETECTION OF PIN HOLES IN TIN PLATE.

By William H. Walker.

Received March 14, 1909.

It is very generally contended among the users of modern tin plate, though not conceded by the makers of the same, that the product now offered upon the market is not so durable as that obtained some twenty years ago. At that time all of our tin plate was imported; but since 1892, or soon after the McKinley Tariff Act was passed, domestic manufacture has steadily grown, until now very little foreign plate is to be found. It is interesting to note that dealers who were previously large importers of tin plate, while maintaining that our present supply is inferior, are willing to admit that even in the "good old times" they were greatly annoyed by the so-called "pin holes" in their goods.

A study of deteriorated tin plate reveals the fact that invariably the tin surface breaks down at a great number of distinct points, and not in continuous patches or zones. The cause of this deterioration is easily seen to be the rusting of the iron (including hereunder steel) base or foundation upon which the tin coating has been placed. These minute bare spots on the iron surface, or small channels through the tin coating down to the iron base are technically called pin holes, and are generally so small as to be undetected by the unaided eye. While unquestionably the number of these holes is greater upon a sheet which carries a very thin coating of tin than upon the triple or quadruple plate, yet upon the heaviest and most expensive plate such as the "dairy stock" used in making large milk cans, the occurrence of these imperfections in the coating is so frequent as to seriously impair the life of the can. Generally the most careful inspection of a heavily coated sheet fails to indicate any lack of continuity of the tin coating, and yet cans made from such stock show rust spots within a few days after being put into service. Contrary to what might be expected, experience demonstrates that the very rough places and apparent imperfections on the bright tin surface are not centers of corrosion, but that rust spots appear at places where the tin coating is seemingly most perfect.

As has already been shown,[1] before iron can form rust it must pass into water solution in the shape of iron ions, and there must at the same time separate from the water or film of moisture an equivalent number of hydrogen ions. Tin is a metal which has a negligible solution pressure, on the one hand, and presents a surface upon which hydrogen can separate and be readily oxidized, on the other. Hence, tin and iron in the presence of water form what is spoken of as a "galvanic couple" or "cell," and an electric current flows from the iron to the tin induced by the solution of the iron and the plating out or precipitation of the hydrogen.

Fig 1

In accordance with this theory, when rust spots form upon the surface of a tin plate, the iron must dissolve at the bottom of the pin holes, and pass in this dissolved condition up through the channels to the surface of the tin where it is oxidized by the air and precipitated as rust. But the oxidation and precipitation by the air is not sufficiently rapid to

[1] *Jour. Am. Chem. Soc.*, **29**, 1257.

be easily followed experimentally. Potassium ferricyanide, however (red prussiate of potash), is a reagent which immediately forms with these iron ions an insoluble precipitate and which is bright blue in color. Hence, if at the opening of these

Fig. 2.

channels or pin holes through the tin coating there be a solution of ferricyanide, a blue spot will develop, and indicate definitely the location of the hole. This solvent action of the water can be greatly hastened by increasing the number of the hydrogen ions, which in turn is brought about by the addition of a very little acid. Disturbances on the surface due to convection currents may be eliminated by stiffening the solution with ordinary gelatine. The proportions which have been found to develop the majority of the pin holes within thirty minutes or so, are as follows:

Gelatine	50 grams
Water	450 "
$K_3Fe(CN)_6$	1 "
H_2SO_4	1 "

The gelatine is dissolved in the water by the aid of heat and the ferricyanide added as the reagent is needed; owing to the gradual reduction of the ferricyanide and the action of the acid on the gelatine, the acid should be added only when the gelatine has cooled to about 40° C., and only so much of the reagent prepared as can be used within a few hours. If a large number of plates are to be examined, the sensitiveness of the reaction may be increased by soaking the plates over night in a dilute ammonium chloride solution, or by dipping them for one-half minute in 5 per cent. sulphuric acid. Either of these treatments loosen the material at the bottom of the pin holes, and allows the iron at these points to dissolve more rapidly.

The number and distribution of the pin holes as found upon an average sheet of "coke plate" is shown in Fig. 1, while a sheet of extra heavy dairy stock appears as in Fig. 2. Not infrequently the holes appear to be on lines, indicating that they

Fig. 3.

may have been caused by a scratch which at places pierced the tin coating, extending down to the iron base. This is well shown in Fig. 3 where the scratches are in curves, suggesting that they were due to the rotating brush used in cleaning the

grease or tallow from the plates, or by moving one plate over another with a twisting motion. Such injuries are seen to be ready centers of corrosion.

In order to determine what proportion of the imperfections brought out by the reagent were due to holes incident to cleaning and handling the plates after tinning, some regular coke sheets were obtained just as they emerge from the tin bath, still covered with the tallow used on the top of the bath. While the number of the holes was reduced, the improvement was not such as to warrant a radical change in the customary method of cleaning. This experiment, however, emphasizes the softness of the tin coating and the great care which must be given to handling tin plate if the centers of corrosion are to be kept at a minimum.

With this easy and accurate method of locating the pin holes or other points on the tinned surface where the iron base is exposed, it is hoped that something more definite may soon be learned regarding the cause of these imperfections and a possible method of preventing them be suggested.

RESEARCH LABORATORY OF APPLIED CHEMISTRY.
MASS. INST. OF TECH.,
BOSTON.

THE CONSUMPTION OF NITRATE OF SODA IN THE UNITED STATES.[1]

By CHARLES E. MUNROE.

Received March 8, 1909.

On November 10, 1904, I had the honor of calling the attention of the members of the Washington Chemical Society to the fact that as the statistics for the chemical manufactures had come to be taken by the Bureau of the Census they could be made use of in solving many problems of interest and value, provided only that they were properly used, and I pointed out that one of these problems was that of ascertaining the principal industries in which a given material was used and the extent of its use in each industry. The results of this process as applied should prove to be not only of general scientific and economic interest, but also of special value in legislation and litigation where the rule of "principal use" obtains; in determining tariffs and levying taxes; in fixing freight rates; in manufacturing and other operations where the question of substitution may arise; and in other special instances. In the investigation work of the census itself such data furnishes additional checks on the returns.

[1] Read at the Baltimore meeting of the American Chemical Society, December 31, 1908

The application of this method was illustrated by taking sulphuric acid as an example, since this is the substance of fundamental importance in the chemical industries, and there was presented, in tabular form, the results obtained. These results, after further checkage, have been published on page 23 of "Chemicals and Allied Products for 1905," this being Bulletin No. 92 of that census of manufactures.

Attention having been called to the proper use of the statistics of the census it may be well to state here that, where the chronology is of importance one should be careful to ascertain the period of time to which any given census statistics refer, because, in a census of manufactures, the data record transactions already completed at the time the investigation was made, and, because of changes in the law, as enacted by the Congress, the yearly periods covered may not be similar and the intervals between the successive censuses may not be of precisely the same length. In illustration we have the census of 1900, covering the operations for the year ending May 31, 1900, and the census of 1905, covering the operations for the calendar year ending December 31, 1904, except for the State of Michigan, where, for the purpose of coöperation with the State authorities, and to avoid duplicate enumeration in the same year, the statistics were collected for the year ending June 30, 1904.

Also it may be proper to point out the chance of error which may arise from making use of census data without consulting the text carefully so as to ascertain to what the data applies. Thus, if one wishes to obtain the statistics for the chemical industries of this country at the census of 1905 he might consult Table CX on page clxxi, of Part I, and find the value of the products given as $1,031,965,263, or he might consult Table 1, on page 398 of Part IV and find the value of the products given as $323,997,131 or a difference of over $707,000,000 in the value of products for the same period of time. But on investigating the tables and their accompanying text we find the first to cover the "Chemical Group" and to embrace a large part of those substances found in chemical technologies, while the second table treats only of those substances styled in the census classification, "Chemicals and Allied Products." Also, to take another example, we find from Table 8, page 404 of Part IV, that the sulphuric acid produced at the census of 1904 was 467,614 tons, while from Table II on page 405 of the same part, the sulphuric acid

produced is reported for the same census as 1,869,437 tons, both being for 50° Bé. acid. From inspection of the text we find there is no discrepancy between these figures, but that the first table treats only of the products of those establishments which are included in the census class of "sulphuric, nitric and mixed acids," while the second table gives the total sulphuric acid produced not only for sale, but for consumption also, by establishments of all kinds.

What is true of products is also true of materials used in manufacture. They may appear in different reports represented by different numbers and yet each of the statements may be correct. Such a condition of affairs may be repeatedly met with in the Reports on Chemicals and Allied Products, and it is here especially, that the text should be scrutinized, since each of the Special Reports for 1900 and 1905 embraces nearly two score of classes and some thousands of industries and, in order to present the true condition of each of several industries, it has been necessary to duplicate some of the data.

Thus if we examine the statistics of the class styled "Fertilizers," we find nitrate of soda enumerated as one of the materials used in this manufacture, and that it is used in this industry not only as a direct component of mixed or compounded fertilizers, but also in the manufacture, within fertilizer factories, of sulphuric acid by the chamber process. Again if we examine the report on the class styled "Explosives," we find that nitrate of soda, as a material used, is used not only as a component of blasting powder and of dynamite, but also in the manufacture, within explosive factories, of nitric acid and also of saltpeter or potassium nitrate. In order then to completely set forth the sulphuric acid, or nitric acid, or saltpeter industries, the quantities of these substances produced in fertilizer or explosives establishments, and of the materials used in their production, must be reassembled and presented anew.

Two methods for presenting the statistics of the consumption or distribution of the materials of manufacture are thus indicated. (1) By the classes of products in the manufacture of which the material is consumed both directly and indirectly. (2) By the products in the manufacture of which the material is consumed directly only though some of these products may constitute the raw material of further manufacture. The data under the first category is that which is reported by the establishments in gross, and may be taken directly from the published census tables. The data under the second category must, on the other hand, be obtained by analyses of the data returned for each class, assigning the proportion of the material consumed in the manufacture of each intermediate and each final product, and then assembling that consumed in the direct manufacture of each single product.

Proceeding in this manner for nitrate of soda, I find:

(1) Nitrate of Soda Consumed in the United States by Establishments Classes as Follows:

Class.	1900. Short tons.	1905. Short tons.
Fertilizer industry	19,518	42,213
Dyestuffs "	223	261
General chemicals industry	35,990	38,048
Glass industry	10,770	11,915
Explosives industry	88,924	133,034
Sulphuric, nitric and mixed acids ind	27,406	29,301
	182,431	254,772

(2) Nitrate of Soda Consumed in the United States Classed by Products in which it is Directly Used.

Products.	1900. Short tons.	1905. Short tons.
Compounded fertilizers	13,058	34,795
Dyestuffs	223	261
General chemicals	30,287	31,324
Glass	10,770	11,915
Explosives	76,696	100,985
Nitric acid	30,213	50,301
Saltpeter	5,703	6,724
Sulphuric acid	15,481	18,467
Total	182,431	254,772

An attempt has been made to check these totals by comparing them with the quantities of nitrate of soda reported by the Bureau of Statistics as having been imported for consumption in the United States during the fiscal years 1899 and 1904 and 1905, taking the average of this latter two-year period. These quantities are reported in long tons, while the census quantities are given in short tons. As reduced we have 206,357 short tons as being available at the Census of 1900 and 322,709 short tons as being available at the Census of 1905. There is therefore 23,926 short tons of nitrate of soda for 1900 and 67,937 short tons for 1905 not accounted for in the tables which may be charged up to all other uses and products, such as enameling, metallurgical flux, pickling and the manufacture of minor chemicals. These last figures must be regarded as mere approximations, since stocks of nitrate are frequently hoarded and then brought out when there is a specially active demand for them, and it may therefore happen that the consumption in this country for a given year may exceed or fall below the imports for that year

The results set forth in the tables, though not exhaustive are of interest, especially in the item of fertilizers, for there is a wide-spread belief that nitrate of soda is most largely consumed in agriculture, yet such does not appear to hold true in this country. But the conditions which obtain in this industry in the United States vary widely from those which obtain in European practice, for, in the United States, besides nitrate of soda and ammonium sulphate, large quantities of other nitrogen-containing substances are used in compounding fertilizers. Thus the statistics of the census of 1905 show that in that census year there was used for this purpose, besides the nitrate of soda, 10,540 tons of ammonium sulphate, 923,305 thousand fish, 125,888 tons of ammoniates, 1,160 tons of saltpeter, $2,376,448 worth of cotton-seed meal and $5,094,149 worth of bones, tankage and offal.

The menace to an extension in the use of nitrate of soda in the United States is found:

(1) In the increased use of by-product ovens for coking coal, it having been shown[1] that but 3,317,585 tons of the 37,376,251 tons of coal coked in this country in the census year 1905 were coked in by-product ovens and that if all had been so treated there would have been produced 359,560 tons of ammonium sulphate instead of 15,773 tons which was the actual yield from this source.

(2) In the substitution of contact processes for chamber processes in the manufacture of sulphuric acid.

(3) In the discovery of calcium cyanamid or lime-nitrogen because an extensive plant is now being erected at Niagara Falls for its production, and

(4) In the introduction of electric processes for the manufacture of nitrates from atmospheric nitrogen.

THE GEORGE WASHINGTON UNIVERSITY

CHANGE IN THE COMPOSITION OF UNGROUND CEREALS DURING STORAGE.[2]

BY SHERMAN LEAVITT AND J. A. LECLERC.

Received March 14, 1909.

The purpose of this investigation was to find out if there is any change in the chemical composition of cereals and to what extent these changes take place when they are stored in their natural state (unground) for a period of months or years. Where many hundreds of samples are to be investigated it is not always convenient to analyze all of the samples when fresh, and as a result some samples are analyzed after they are months and in some cases even a year or more old.

It would seem possible that a deterioration or a transformation of some of the organic compounds such as carbohydrates or proteins might easily take place either due to the direct loss through respiration of carbon dioxide producing simpler compounds or to an actual conversion of one compound into another, such as starch into sugars due to enzymic action.

The authors are not aware that very much work along this line has been carried out in the past. The effect of ageing has been studied in connection with the gluten content of the grain[1] (good wheats maintaining their gluten content better than poor wheats), but as far as we know the study has not been applied to the different combinations of nitrogen in the grain such as the proteins and amids nor to the content of sugars.

In the fall of 1906 large samples were collected of the season's crop of four cereals, *i. e.*, field corn, Swedish select oats, Kubanka wheat and Minnesota No. 6 barley, all grown at the State Experiment Station at Brookings, South Dakota, and were sent to the Bureau of Chemistry for experimentation. Small samples of these were ground and analyzed immediately for the following substances: Water; ash; P_2O_5; total nitrogen; albuminoid nitrogen; 70 per cent. alcohol-soluble nitrogen; 5 per cent. K_2SO_4-soluble nitrogen; water-soluble nitrogen; water-soluble nitrogen coagulable on heating; water-soluble nitrogen precipitated by cupric hydroxid (Stutzer's reagent); invert sugar; cane sugar as dextrose; weight per 1000 kernels; and weight per bushel. *All results* with the exception of the last two have been calculated to the *dry basis*. The samples have been ground and analyzed at intervals of six months and the results compared. In the fall of 1907 additional samples of wheat, oats and barley were collected at College Park, Maryland, at the Experiment Station. Rye was also taken as an additional cereal. The record of corn is a continuous one for two years involving five separate periods of analysis. A sample of ground corn was allowed to stand for one year and its

[1] Bulletin No. 65. Census of Manufactures, 1905. Coke

[2] Read before the Baltimore meeting of the American Chemical Society on December 30, 1908 and published by permission of the Secretary of Agriculture.

[1] "La Dégénérescence des Blés," L. Vuaflart, *Jr. Agr. Prac.*, 1908, No. **40**, page 429.

analysis compared with the sample that had stood unground for one year.

TABLE I.

Ground October, 1906.
Analyzed October, 1906.

Cereal.	Sugars. Invert, per cent.	Cane, per cent.	Total, per cent.
Corn	0.43	1.73	2.16
Barley	0.63	2.26	2.89
Oats	0.50	1.05	1.55
Wheat	0.55	2.21	2.76
Rye	..	..	..

	Nitrogen soluble in		Water.	
	70% alcohol, per cent.	5% K_2SO_4, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn	0.65	0.24	0.17	0.09
Barley	0.62	0.46	0.28	..
Rye	..	..	..	..
Wheat	1.07	0.51	0.14	..
Oats	0.47	0.42	0.36	..

Ground October, 1907.
Analyzed October, 1907.

Cereal.	Sugars. Invert, per cent.	Cane, per cent.	Total, per cent.
Corn	0.26	0.10	0.36
Barley	0.94	1.70	2.64
Oats	0.38	0.96	1.34
Wheat	0.53	2.16	2.69
Rye	..	..	..

	Nitrogen soluble in		Water.	
	70% alcohol, per cent.	5% K_2SO_4, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn	0.58	0.21	0.20	0.14
Barley	0.62	0.51	0.35	0.18
Rye	..	..	..	..
Wheat	0.98	0.48	0.10	0.23
Oats	..	..	..	..

Ground October, 1907.
Analyzed October, 1907.

Cereal.	Sugars. Invert, per cent.	Cane, per cent.	Total, per cent.
Corn	0.35	0.41	0.76
Barley	0.66	1.37	2.03
Oats	0.52	0.82	1.34
Wheat	0.32	2.17	2.49
Rye	0.62	4.39	5.02

	Nitrogen soluble in		Water.	
	70% alcohol, per cent.	5% K_2SO_4, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn	0.52	0.21	0.17	0.11
Barley	0.45	0.33	0.32	0.23
Rye	0.59	0.56	0.70	0.43
Wheat	0.92	0.55	0.14	0.31
Oats	0.40	0.34	0.32	0.22

Ground in October, 1908.
Analyzed October, 1908.

Cereal.	Sugars. Invert, per cent.	Cane, per cent.	Total, per cent.
Corn	0.40	0.29	0.69
Barley	0.66	1.42	2.08
Oats	0.61	0.88	1.49
Wheat	0.40	1.91	2.31
Rye	0.86	4.24	5.10

	Nitrogen soluble in		Water.	
	70% alcohol, per cent.	5% K_2SO_4, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn	0.34	0.18	0.12	0.08
Barley	0.43	0.35	0.32	0.14
Rye	0.61	0.65	0.58	0.24
Wheat	0.91	0.55	0.13	0.24
Oats	0.36	0.35	0.32	0.18

In studying these two sets of analyses in Table I, giving yearly results, we notice that the change in the sugar content of the ground corn is more marked than in the unground sample. The total sugar content of the original sample was 2.16 per cent.; after standing ground one year it was 0.36 per cent., whereas the sample that was freshly ground showed 0.76 per cent. We see from these results that about 80 per cent. of the total sugar in corn is lost in one year's time when ground, while about 60 per cent. of the total sugar content is lost on standing even without grinding.

We also notice that the alcohol- and water-soluble nitrogen compounds of corn both show a tendency to decrease with age, the alcohol-soluble decreases 50 per cent. in two years, whereas the total nitrogen remains practically constant. This would seem to indicate a slight change in the protein bodies themselves, involving some rearrangement of these complex molecules.

The alcohol-soluble protein bodies of wheat seem to indicate the same tendency to decrease with age as is exhibited in the case of corn but not to so great an extent. The sugar content of the wheat behaves quite differently from corn in many cases, although the sample of wheat which has been specially preserved for the ageing process indicates a slight falling off in the sugar content at the end of the first and second years. After the first year the tendency in many instances is to increase. This tendency to increase was shown by regrinding and reanalyzing fourteen samples of wheat which had been analyzed two years previously; in all but one a marked increase in the content of total sugar was observed, this being from 1–24 per cent. in the total sugar content.

TABLE II.

Sample.	Moisture content, 1906.	Moisture content, 1908.	Cold extraction. Total sugar, 1906.	Total sugar, 1908.	Dry basis, cold extraction. Total sugar, 1906.	Total sugar, 1908.	Percentage increase in sugar content
742	11.17	9.17	2.90	3.34	3.27	3.68	11.1
743	10.31	8.70	3.17	3.88	3.53	4.25	17.0
747	11.11	9.75	2.36	2.45	2.65	2.71	2.0
752	7.91	9.37	3.42	3.34	3.71	3.69	—0.5
757	9.55	8.90	2.70	2.90	2.98	3.18	6.3
760	9.31	9.46	2.40	3.14	2.65	3.47	23.6
763	9.02	9.86	2.37	3.09	2.61	3.43	24.0

In studying the sample of oats (see Table I) we find a similar change to that of corn but a more gradual one. The total sugar content has fallen off about 12 per cent. of the total sugar originally present. In barley we observe a tendency of the alcohol-soluble, salt-soluble, and the water-soluble protein bodies precipitated by Stutzer's reagent to decrease.[1] The total sugar also shows an appreciable loss.

Rye in the course of one year shows a very slight tendency to increase its alcohol- and salt-soluble protein,[1] while its water-soluble protein coagulated by Stutzer's reagent has lost about 50 per cent. The total sugar has remained practically constant, the only apparent change being an increase in the invert sugar.

At this point the authors did considerable work to determine the best method of extracting sugars from grains with the least amount of enzymic action. Extraction with boiling water kept at the boiling temperature for one hour although very troublesome on account of the gelatinization of the starch and its difficult filtration was referred to as the standard method. Assuming that the treatment with boiling water inhibits enzymic action and using this method as a standard we find that extraction with water previously cooled to 5–7° C. and kept at this temperature during the entire extraction gives results for total sugar almost identical with the ones obtained by the boiling water extraction. The results obtained by this method for total sugar are three or four tenths of 1 per cent. lower than by extraction with water at room temperature, the high results being probably due to diastatic action.

At the suggestion of Dr. C. S. Hudson, of the Bureau of Chemistry, we tried extracting the sugars with a 0.2 per cent. solution of sodium carbonate at room temperature. The results for total sugar agreed excellently with those obtained by the cold extraction, the latter method being used for all sugar determinations on ageing.

[1] The changes in the protein combinations of barley, rye, wheat and oats in two years' time is so small that we do not wish to lay stress upon them. Corn, however, is an exception.

The presence of a 0.2 per cent. solution of sodium carbonate seems to entirely stop enzymic action in water infusions of cereals. The samples examined did not show the slightest trace of reducing sugars when sodium carbonate was used. (Care must be observed to see that the solution be not acidified during the process of digestion and clarification.) The total sugars, however, were the same as by the cold extraction. Water at 5–7° C. seems to be unfavorable to diastatic action.

Germination tests were made of all of these grains in December, 1908, by Dr. E. Brown, botanist of the Seed Laboratory of the Bureau of Plant Industry, U. S. Department of Agriculture, in which he obtained the following results on one hundred seeds of each of the grains submitted:

TABLE III.

	Duration of test	Per cent germination.
Corn	5 days	0.0
Oats	6 "	55.0
Barley	6 "	29.5
Rye	6 "	0.0
Wheat	6 "	0.0

The germination tests are included as they may possibly help to explain some of the changes that have taken place. It has been suggested that loss of germination power by cereals during storage may bear some relation to its sugar content.

In conclusion, we would say that our results for the period of time they represent (two years) seem to indicate that there is more or less change in all cereals under the influence of ageing. These changes seem to take place whether the cereal is stored in the whole grain or is ground to a fine powder before storage. In the latter case, however, the changes take place more rapidly. We notice that the principal products which seem most susceptible to change are first the sugars and then the 70 per cent. alcohol-soluble proteins, the 5 per cent. K_2SO_4-soluble proteins and the water-soluble proteins coagulated by so-called Stutzer's reagent.

Corn, barley and oats are most subject to loss of sugar during ageing. On the other hand, many samples of wheat show a slight loss the first year and then quite a rapid gain in the sugar content, in some cases a gain of 24 per cent. of the total sugar present being noted at the end of two years.

Considering the grains most susceptible to protein change we have in the order given corn and to a very slight degree barley, rye, wheat and oats. As we should expect, there seems to be no

change in the mineral constituents of the grain or in the total nitrogen, the weight per bushel and the weight per 1000 kernels remaining practically constant.

Laboratory of Vegetable Physiological Chemistry,
Bureau of Chemistry, Washington, D. C.

A RAPID METHOD FOR THE DETERMINATION OF TOTAL POTASSIUM IN SOILS.

By O. M. Shedd.

Received March 8, 1909.

The method herein described was devised for the rapid determination of total potassium in soils, but is applicable to silicates generally. It is a combination of the J. Lawrence Smith[1] method with the cobaltinitrite method of W. A. Drushel,[2] the potassium being brought into solution by the former method and determined by the latter, without previous separation of the calcium.

The procedure recommended is as follows: One gram of finely ground soil and an equal weight of C. P. ammonium chloride are well mixed by grinding them together in a mortar and these intimately mixed with 8 grams of C. P. calcium carbonate. The mixture is transferred to a platinum crucible of 25–50 cc. capacity, in which a thin layer of calcium carbonate has been sprinkled to prevent sticking of the fused mass to the bottom, and the contents compacted by gently tapping the crucible. The crucible is then covered with a well-fitting lid and supported upright over a good burner by means of a square of asbestos board through which a round hole has been cut of such size that about one-third of the crucible projects below the board and will be exposed to the heat. The heating is conducted as recommended by Smith as given in the detailed description of the process already cited. By this arrangement only the part of the crucible containing the mixture is exposed directly to the flame, while the upper part and cover are kept relatively cool, thus reducing to a minimum the chance of osing potassium chloride by volatilization. After the heating has been finished and the crucible is cool, the sintered mass is transferred to a porcelain evaporating dish, rinsing lid and crucible into the dish with hot water, adding, finally, about 50 cc. It is best to let the mass slake a few minutes with only enough water to moisten it, after which it should be well ground up with a pestle, more water added and allowed to

[1] Fresenius' "Quantitative Analysis," Am. edition, page 426.

[2] Adie & Wood, *J. Chem. Soc.*, **77**, 1076. Drushel, *Am. J. Sci.*, **24**, 433; *Chem. News*, **97**, 124.

digest on the water-bath two or three hours. The liquid is now decanted through a filter and the mass stirred up with another portion of hot water, allowed to settle a few moments, decanted again and this operation repeated two or three times, after which it is transferred to the filter and well washed, using about 200 cc. of hot water. It is not necessary or practicable to wash free of chlorides. Indeed, in one experiment a faint test for chlorides was still obtained after washing with a liter of boiling water. The liquid, or an aliquot containing about 0.01–0.02 gram of K, is put into a porcelain casserole or dish, acidified slightly with acetic acid and evaporated to a volume of about 10 or 15 cc.[1] Ten cc. or a liberal excess of the cobaltinitrite reagent, prepared according to Adie and Wood,[2] are added slowly, so that the precipitate may not be too finely divided, and the liquid evaporated on the water-bath to a syrupy consistency becoming solid on cooling. It is important not to heat longer than is just necessary. After cooling, the soluble matters are dissolved in about 25 cc. of cold water which should give a brown solution, showing excess of reagent, and the solution decanted through a carefully prepared Gooch filter[3] and this operation repeated until the dish and any precipitate remaining in it have been thoroughly washed.[4] After washing the filter, the felt with the precipitate is returned to the dish in which the precipitation was made and well broken up by stirring with a glass rod in a little water. If any of the precipitate adheres to the Gooch crucible so that it cannot be washed off, the crucible also is to be put into the dish. A measured excess of N/10 potassium permanganate solution (usually 20–40 cc.) is now run in and the whole diluted to about 8 or 10 times the volume of permanganate added, the dish covered and its contents heated nearly to boiling over free flame or hot plate, with frequent stirring, for about ten minutes, or until the potassium cobaltinitrite is thought to have been completely oxidized. It was found that the oxidation requires a somewhat longer time than the five to eight minutes recommended by Drushel, apparently because it is hard to separate the yellow potassium precipitate from

[1] When the reagent is added to a dilute solution, it is decomposed before the potassium salt is precipitated. In small volumes, this does not happen.

[2] Sutton's "Volumetric Analysis," 9th edition, p. 62.

[3] The asbestos pulp for making the felt should be just fine enough to hold the precipitate and free from very fine particles.

[4] A half-saturated solution of common salt may be used instead of water, if there is trouble in filtering the precipitate.

the asbestos, so that the permanganate can come in contact with it. When the oxidation is thought to be complete, as indicated by the darkening of the solution and separation of manganese hydroxide, about 15 cc. of dilute sulphuric acid (1 : 7) are added and allowed to act three or four minutes to favor oxidation of the last traces of cobaltinitrite.[1] A measured excess of N/10 oxalic acid containing 50 cc. of concentrated sulphuric acid to the liter is then run in and the liquid kept at the same temperature until all the manganic hydrate has been dissolved and the solution is colorless. At this point it will be seen by the absence or presence of the yellow potassium compound, whether the oxidation of the cobaltinitrite precipitate was complete. The excess of oxalic acid is now titrated with N/10 permanganate solution. The total volume of permanganate solution used, less that equivalent to the oxalic acid added, gives the amount used up in oxidizing the cobaltinitrite and this, multiplied by the appropriate factor, gives the weight of potassium obtained. One cc. of N/10 permanganate solution is equivalent to 0.000711 gram K, or 0.000856 gram K_2O. It is necessary, also, to carry out a blank experiment, under the same conditions as the analyses, using the same quantities of the reagents, and to subtract the small amount of permanganate solution consumed from that found in the analyses. The following determinations have been corrected in this way. The permanganate used was standardized by means of Kahlbaum's special C. P. sodium oxalate and also by iron wire, the two methods giving identical results. The soils analyzed were the two samples sent out for coöperative work in 1908 by the Referee on Soils of the Association of Official Agricultural Chemists, and were selected for testing this method because a number of determinations had already been made upon them in this and other laboratories by the J. Lawrence Smith method and by Pettit and Ystgard's modification of that method.[2] The following table gives the results obtained by the new method, in the columns headed "volumetric," in comparison with determinations by the J. L. Smith method and the average of some twelve to fourteen determinations by Association chemists, in the columns headed "gravimetric."

[1] The sulphuric acid is not to be added first, along with the permanganate, as the action would be very rapid and some cobaltinitrite might escape oxidation.

[2] Proceedings A. O. A. C., 1906 (Bureau of Chem., Bull. **105**) page 147, also U. S. Dept. Agr., Bur. of Chemistry, Circular No. **34**, p. 4.

PERCENTAGE OF K, CALCULATED ON THE WATER-FREE SOIL.

	Sample No. 1.		Sample No. 2.	
	Volumetric	Gravimetric	Volumetric	Gravimetric.
1 1 gram of soil taken....	1.14	..	1.47	..
2 1 gram of soil taken.............	1.14	..	1.46	..
3 1 gram of soil taken.............	1.22	..	1.47	..
4 ½ gram of soil taken...........	1.17	..	1.43	..
5 ½ gram of soil taken...........	1.23	..	1.46	.
6 1 gram taken, solution divided...	1.12	1.07	1.60	1.45
7 1 gram taken, solution divided...	1.12	1.07	1.65	1.46
8 1 gram taken, solution divided...	1.10	1.14	1.37	1.44
9 1 gram taken, solution divided...	1.12	1.10	1.50	1.50
Average....................	1.15	1.10	1.49	1.46
A. O. A. C. average, Smith method..	..	1.18	..	1.56
A. O. A. C. average, Pettit and Ystgard modification..........	..	1.17	..	1.56

In Experiments 6, 7, 8 and 9, 1 gram of soil was treated by the Smith method as far as obtaining the solution. This was then divided into two equal parts, one-half being used for determination of potassium, as already described, and the other by the regular gravimetric method. In this way irregularities in the decomposition of the silicates would be eliminated from the comparison.

A good degree of concordance is found in the average results of all the determinations by the three methods, though there is not as close agreement as could be desired between the several findings by the new method, especially in soil No. 2, the difference between the lowest and highest being 11 per cent. of the average in soil No. 1, and 19 per cent. in soil No. 2. The low result in Experiment 8 of soil No. 2 has not been accounted for, but it is believed that the high results in Experiments 6 and 7 on the same soil were caused by too long heating of the residue after evaporation with the nitrite reagent. In these two instances the dishes were, through oversight, left on the water bath two or three hours. When the residue is heated too long, especially when the solution has not been sufficiently concentrated before the nitrite reagent is added, the yellow potassium precipitate becomes contaminated with small quantities of a bluish-green substance probably containing cobalt, which washing with water does not remove. Under these circumstances, the results appear to be too high. This source of error should be carefully guarded against also in the blank experiments. The potassium equivalent to permanganate reduced in 9 blank experiments with reagents only ranged from 0.10–0.23 per cent. K, calculated for 1 gram portions, the average being 0.1567 K, a variation great enough to introduce a very considerable error, showing that the greater

part of the reduction was not due to potassium in the reagents.

Two control experiments made with the quantities of reagents used for 1 gram of soil, dividing the solutions from each into two equal parts and adding 0.0175 gram of C. P. K_2SO_4 to each of two of these portions gave, in the halves to which no potassium had been added, 3.2 cc. and 1.65 cc. of permanganate solution reduced. In the corresponding halves, after subtracting the equivalent of the potassium added from the total volume of permanganate solution reduced, there remained 1.51 cc. and 1.24 cc. respectively, a much more satisfactory result. The plan of adding a known quantity of potassium to the control will probably give more reliable results than are obtained without this addition. These and other points affecting the accuracy of the method will be investigated further.

It is believed that these sources of error can be controlled and that the method is a promising one for rapid work, where many determinations are to be made at the same time. It has the advantages of easy manipulation, rapidity, requiring only about half the time necessary for the Pettit-Ystgard modification, and cheapness of reagents used as compared with platinum chloride.

It is self-evident that the method is of as general application to silicates as that of Smith, but it has only been tried upon soils.

POTASSIUM, AS PER CENT. OF THE WATER-FREE SOILS.

	Sample 1.		Sample 2.	
Analyst.	Pettit-Ystgard modification.	Smith method.	Pettit-Ystgard modification.	Smith method.
A. W. Gregory, Illinois...	1.156	1.205	1.568	1.582
	1.157	1.175	1.547	1.598
	1.182	1.164	1.566	1.594
	1.156	1.208	1.552	1.586
	1.158	1.223	1.547	1.566
W. B. Ellett, Virginia....	1.068	1.183	1.495	1.564
	1.081	1.121	1.487	1.536
S. D. Averitt, Kentucky.	1.190	1.162	1.552	1.491
	1.185	1.170	1.546	1.541
	1.214	1.202	1.531	1.565
O. M. Shedd, Kentucky..	...	...	...	1.510
	...	...	...	1.630
R. F. Trowbridge, Missouri	1.177	1.186	1.512	1.357[1]
A. A. Wells, Iowa........	1.271	1.121	1.608	1.751[1]
	1.275	1.134	1.702[1]	1.760[1]
I. O. Schaub, Iowa......	1.320[1]	...	1.656	...
	1.440[1]	...	1.678	...
Average............	1.175	1.166	1.560	1.563

As the proceedings of the Association of Official Agricultural Chemists for 1908 may not appear for several months, it will be of interest to publish here in detail the results obtained on these soils by the several chemists coöperating, using J. L. Smith method and the Pettit-Ystgard modification.

[1] Not included in the average.

The difference between the highest and lowest result, included in the averages, is 18 per cent. of the average in No. 1, and 12 per cent. in No. 2, by the modified method and 9 per cent. in each sample by the regular Smith method.

The author desires to express his thanks to Dr. A. M. Peter, of this Station, for many valuable suggestions made during the progress of the work.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,
LEXINGTON, KENTUCKY.

LOSS OF POTASH IN COMMERCIAL FERTILIZERS.[1]

BY F. B. PORTER AND E. G. KENNY.

Received January 15, 1909.

It is a well-known fact that at the present time there is an apparent loss of water-soluble potash, added to commercial fertilizers, when determined by the method of the A. O. A. C. This is due to the fact that acid phosphate, like clays and soils, has a certain power of withdrawing certain soluble compounds from solution. It was with the hope of learning more about this retention of potash that the following work was attempted. Our thanks are due to Mr. G. S. McDaniel for a part of the analytical work here reported.

The loss is purely a laboratory matter, being due to the solvent used in the analytical method. The Lindo-Gladding method[2] recognized as official by the Official Association of Agricultural Chemists requires "with potash salts and mixed fertilizers" the boiling of "10 grams of the sample with 300 cc. water thirty minutes."

A short review of the recent work of the association is to the point here. The 1901 and 1902 reports of the potash referee showed a loss of 8 per cent. and 7 per cent. respectively of the water-soluble potash added in making mixed fertilizers when the official method was used.

The addition of 5 cc. of hydrochloric acid was suggested as a means of freeing the potash. This was tried by the association for two years and recommended as an addition to the official method by the referee at the 1904 meeting. The modified method gave results much nearer the calculated amount added as shown by the following table:

[1] Presented before the Division of Fertilizer Chemists, Baltimore, December 31, 1908.

[2] Bureau of Chem., Bull. 107, p. 11.

Average of the work of seventeen analysts.[1]

	Sample No. 1 phosphate potash.	Different from theory.	Sample No. 2 ammoniated fertilizer.	Different from theory.
Calculated potash......	4.31	..	4.30	..
Official method........	3.90	—0.41	4.05	—0.25
Modified method.......	4.23	—0.08	4.33	—0.03

Action on the recommendation was postponed until the next year. At the 1905 meeting the referee reported similar results and investigated the possibility of the use of the acid solvent opening up the way for the use of potash silicates as fillers. His conclusion was "the amount of potash that could be so added is insignificant."[2] He also found that the laws of twenty-seven states require and specify water-soluble potash and largely because of this fact the motion to make the addition of 5 cc. of acid official, was lost.

Since that time Mr. Cushman's work on potash in feldspars has been made public and he has suggested to the association that it make a study of what really constitutes available potash in soils and fertilizers and ground mineral products so that we may have a definition of available potash.[3] No work has to our knowledge been done along this line as yet although the work of the Bureau of Soils on Absorption of Phosphates and Potassium by Soils[4] will be valuable material when the work is begun.

Our work besides confirming the loss above reported comprises a study of the conditions affecting the retention of the soluble potash and a study of the ease with which the retained potash is liberated.

The results given above which Mr. F. B. Carpenter as referee reported to the A. O. A. C. indicate that the retention of potash is a property inherent in the acid phosphate as retention is highest in phosphate and potash goods. We have found this to be the case as will be clearly shown by the results given later which also show the effect of various kinds of phosphate. Practically all the results given are confirmatory of the fact that potash is retained, so to avoid duplication they will not be given at this point.

A study of the factors affecting the retention of potash reveal the following points:

1. Acid phosphates of different ages and from different kinds of rock so far as tested show practically the same retention. The figures given are the average of duplicate determinations. The weighed phosphate and muriate of potash were introduced into 500 cc. flasks, a little water added, allowed to stand for about an hour and then the determination completed according to the official method, boiling thirty minutes with 300 cc. water, etc.

Acid phosphate.

Wt. in grams.	Potash present in.	Kind of rock used in making.	Age in months.	Potash theory.	Potash found.	Retained, per cent.
7.00	0.19	Blue Tenn..........	6	9.97	9.71	0.26
7.00	0.11	Brown Tenn........	4	9.89	9.66	0.23
7.00	0.12	Fla pebble..........	2	9.90	9.64	0.26
7.00	0.10	Low-grade Tenn.....	5	9.88	9.65	0.23
7.00	0.14	Low-grade Tenn.....	18	9.92	9.70	0.22
7.00	0.11	Low-grade Tenn.....	4	9.89	9.61	0.28

The approximate factory guarantee for the above would be 10–0–10.

2. The amount retained increases with high percentages of potash.

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	Approx. factory guarantee.[1]
6.45	1.10	1.07	0.03	10–0– 1
6.45	2.10	2.08	0.02	10–0– 2
6.45	4.10	3.98	0.12	10–0– 4
6.45	6.10	5.91	0.19	10–0– 6
6.45	10.10	9.81	0.29	10–0–10

In these experiments the flasks stood one hour after the dry phosphate and muriate had been thoroughly mixed. 200 cc. water was then added and the test allowed to stand another hour. A comparison of these results with the table immediately following, shows that this procedure gave less retention than was obtained when the 200 cc. water was replaced by 10 cc. as was the case in the latter table.

3. The amount retained increases with the amount of acid phosphate present.

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	Approx. factory guarantee.
2.58	4.04	3.99	0.05	4–0–4
5.16	4.08	3.92	0.16	8–0–4
6.45	4.10	3.85	0.25	10–0–4
7.24	4.12	3.80	0.32	12–0–4
9.04	4.14	3.81	0.33	14–0–4

4. Acid-free dried phosphate still retains potash. Acid phosphate was extracted with absolute alcohol to remove free acid and moisture and then dried to remove alcohol. Seven grams of this material in a flask as above reduced a theoretical percentage of 5.45 to 5.28 or a retention of 0.17 per cent. This figure may be low, as the theoretical percentage was calculated on the supposition that the alcohol

[1] *Bull.* **90,** p. 109, Bureau of Chem.
[2] *Bull.* **99,** p. 137, Bureau of Chem.
[3] *Bull.* **105,** p. 194, Bureau of Chem.
[4] *Bull.* **32,** Bureau of Soils.

[1] In the factory guarantees, the first figure refers to available phosphoric acid, the second to ammonia, the third to water-soluble potash.

extracted the small amount of soluble potash contained in the original acid phosphate.

5. The higher the concentration of potash the quicker the retention takes place. Parallel tests in flasks as above, allowing three hours' contact with 10 and 100 cc. of water, gave the following results:

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	cc. water.	Approx. factory guarantee.
7.13	10.11	9.65	0.46	10	11-0-10
7.13	10.11	9.78	0.33	100	11-0-10

6. Ground phosphate rock retains potash. Ten grams of brown Tenn. rock retained 0.18 per cent. potash. The percentage found was 9.65, while the percentage added was 9.83. This rock contains some clay, so it remains an open question whether either the fluoride or phosphate of calcium in the natural state retains potash.

7. A part of the loss of potash is due to the precipitate produced by ammonia and ammonium oxalate. 7.13 grams acid phosphate were boiled with 300 cc. water and filtered into a 500 cc. flask, the potash was then added and to the filtrate the usual precipitants were also added.

	Per cent.
Potash present	10.10
Potash found	9.95
Potash lost	0.15

8. Number 1 tankage shows practically no tendency to retain potash. Ten grams were boiled with the muriate of potash as above.

Potash present	10.19
Potash found	10.18
Potash lost	0.01

9. Number 1 tankage partially prevents the retention of potash. Four grams of tankage added to determinations which were in all other ways duplicates of those given under (1) gave a retention of 0.18 per cent. instead of an average of 0.25 per cent. shown in No. 1. This agrees with the results of the A. O. A. C. above quoted which show 0.41 per cent. loss on phosphate and potash and only 0.25 loss on ammoniated goods. This same point is proven by the table given under (10).

10. Retention reaches a maximum in stored goods. We have shown above that with 10 cc. water, we get a high retention in one hour but just how long it takes to get the maximum loss under factory conditions we have not determined but believe it requires several days. The following results show that there is no further loss in six months on samples a little over a month old.

Approx. factory guarantee.	Per cent. water-soluble potash 5/1/08	10/1 08.	Pot. in insol. Residue (fusion).	Per cent. potash retained	Average per cent. potash retained.
12-0-4	3.27	3.28	0.36	0.36	Acid potash
10-0-4	3.65	3.65	0.37	0.37	
8-0-4	3.35	3.40	0.34	0.34	
10-0-2	1.66	1.67	0.33	0.33	0.35
8-2-2	2.07	2.06	0.26	0.17	Ammoniates
8-3-3	2.94	3.02	0.28	0.19	
8-4-4	3.73	3.83	0.27	0.18	0.18

In this last table we have attacked the problem in another way. Fusing and determining the potash in the dried water-insoluble residue by the J. Lawrence Smith method and deducting the water-insoluble potash known to be present in the tankage in the case of ammoniated fertilizer we have obtained the potash retained in samples whose exact potash content was not known. The general agreement of results obtained by the two methods is good. Blanks were made on the chemicals used in both cases.

The above results bear out the supposition previously held that the retention of potash is not due in any marked degree to the formation of a chemical compound, but is nothing more nor less than happens to a larger percentage of the potash when it comes in contact with the soil, as shown by the work of Schreiner and Failyer in *Bull. 32, Bureau of Soils*.

The ease with which the retained potash is freed is indicated by the following results:

Approx. factory guarantee.	Potash in insoluble residue (fusion).	Potash in residue soluble in neutral ammonium citrate.	Potash in residue soluble in per cent. citric solution.	Potash in residue soluble in water
12-0-4	0.36	0.21	..	0.07
10-0-4	0.37	0.20	0.23	0.11
8-0-4	0.34	..	0.30	..

We feel safe in concluding from these figures that about 25 per cent. of the retained potash is liberated by the first contact with rain water and about 56 per cent. by the first contact with the soil solution. As a comparison Mr. Cushman's results on feldspars show only 0.025 per cent. of the total weight liberated by one extraction with water. We have therefore in the retained potash not an insoluble valueless form but a form readily available to the plant long before the plant has used the part shown in the water-soluble test, and it is probable that in soils deficient in clay this retained form is of even greater value because it will in a measure resist the wasteful leaching processes until the plant has need of it.

The six states, Alabama, Georgia, Louisiana, Tennessee, North and South Carolina, could, under

their present laws, adopt the plan of reporting all of the available potash as shown by some modified method, and in so doing hasten the time when other states would change their laws.

The laws of the other twenty-seven states mentioned by the 1905 referee are probably modeled, as Mr. Booker has said, after the Massachusetts law "which was framed back in 1873 before we had experiment stations, when the idea was that only water-soluble materials were available."

LABORATORIES.
SWIFT FERTILIZER WORKS.
ATLANTA, GA., AND WILMINGTON, N. C.

ADDRESSES.

COAL ANALYSIS[1]

BY N. W. LORD.

Within the last few years the subject of coal analysis has become of great importance to many lines of industry. The demand for the analysis of coal has come from a great variety of sources and largely from those having little acquaintance with chemical methods and the interpretation of chemical results. The chemists, on the other hand, have been compelled to take such methods as were found at hand, and the result of these conditions has been not altogether satisfactory in many ways.

If we consider somewhat in detail the various determinations made in the laboratory in connection with coal testing, it will be easy to show how much is commercial and how little what might be called scientific. The so-called analysis of a coal is usually a practical test of purity of the material on a small scale, but it also involves determinations which are supposed in some way to indicate the nature of the coal itself.

To illustrate, suppose we consider an ordinary sample of bituminous coal. It may be assumed to consist, first, of an organic constituent composed of vegetable residues more or less altered but retaining traces of its original woody structure and composite character and containing as an integral part certain inorganic components. Like its source, woody fiber, it absorbs moisture in damp weather and gives it up in dry weather. The ultimate chemical composition of this material varies with the extent of the alteration, as shown in the peats, lignites and bituminous and anthracite coals, and also, in all probability, with the nature of the vegetation from which it has been derived. This extremely complex and indefinite material may be called "coal substance" for want of a better term. Intimately mixed with this are inorganic substances, probably mechanically introduced with the original vegetable débris or else precipitated by secondary reactions from circulating waters. These may be in the nature of clays or fine sand and also intimately mixed iron pyrites. I have examined samples of coal under the microscope, in which microscopic crystals of pyrites were scattered through the mass in sufficient amount to give high percentages of sulphur in the total, yet in which a superficial examination of the coal itself practically showed no pyrites to the unaided eye. Other minerals may be present in the same way, even such unusual constituents as zinc blend, and, as Dr. Hillebrand has shown, considerable percentages of vanadium sulphide. The extremely complex nature of the organic constituents themselves may be inferred from the variable but sometimes very large amounts of sulphur they contain, well shown in the case of certain peats.

Now in addition to this base constituting the principal part of the sample submitted to the chemists for analysis, it has secondly, more or less coarse admixture of slate, clays and other rock-like material occurring in connection with the deposits of coal and not properly separated in mining, bone coal, and also streaks of cannel and other associated materials, coal-like in character, but differing notably even in the organic material they contain from the coal itself. The fact that many of these ingredients on standing or exposure to air rapidly alter by absorption of oxygen, evaporation, etc., makes it appear that the problem is still further complicated.

Now some of the things that the users of coal wish to know and for which they turn to the chemical analysis in the hope of receiving information are the following: the heating power of the coal; the amount of ash or inorganic matter left on burning the coal; the nature of the combustion of the coal, whether flaming, smoking, rapid, or slow; the gas-producing quality of the coal both as to yield and as to the nature of the gas; the nature of the ash yielded by the coal, whether fusible or not; the amount of sulphur the coal contains; the coking quality of the coal and the purity of the coke produced; and the possibilities of improving its quality by coal washing.

In addition to the above are many questions of special character, such as the nature of the coal substance, the relation of its composition to the previous geological history of the deposit, and the relation of total heating power to the heating power actually available for techincal operations.

What are the analytical methods at present used in the laboratory to meet this series of questions and to handle this very complex material? Most of the laboratory work is done upon a sample which represents or is intended to represent the average composition of the material and which in no way recognizes the separate constituents of the very complex mineral aggregate of which it purports to be an average. The methods therefore give results only approximately related to the coal substance and difficult of general application.

We have as of generally recognized importance the ultimate analysis as ordinarily made, giving the determination of the hydrogen, the carbon, the nitrogen and the sulphur and the percentage of ash left after burning. This analysis also includes an estimate of the oxygen by difference, which is of course only approximate, and has been frequently pointed out in discussions of the subject. This ultimate analysis is capable of a high degree of accuracy for certain elements, which I think could be safely stated as within 0.05 per cent. in the case of hydrogen and perhaps 0.3 per cent. on carbon, 0.03 per cent. on the nitrogen and 0.05 on the sulphur. I do not mean that closer results are not obtainable, but ordinary work in the laboratory by competent chemists would, I think, run within

[1] Read at the Illinois Fuel Conference, Urbana, Ill., March 13, 1909.

these limits. The value of the ultimate analysis in all technical applications of the coal consists in its giving a reasonably accurate basis for the calculation of products of combustion and for comparisons with the heating power of the coal otherwise determined. The weakest point in the ultimate analysis is the uncertainty of its connections with the actual composition of the organic material as distinct from the impurities. Carbon, hydrogen and sulphur are present occasionally as carbonates, as combined water and as sulphates, respectively, in the slates and other mechanical admixtures, and the ultimate analysis does not distinguish between such occurrence and that in the coal substance. Ingenious efforts to eliminate these uncertainties as affecting the heating power by examination of various samples of the same coal differing widely in percentage of mechanical impurities have been made by several chemists.

In addition to the ultimate analysis, we have the more commonly made "proximate analysis," consisting of the determination of the moisture, ash, fixed carbon and volatile combustible matter in the coal. Much has been written in regard to these determinations.

On the same sample of coal closely agreeing results can be obtained on the ash and fairly close on the moisture. The variations in the volatile combustible is much larger and can only be kept within reasonable limits by very careful adherence to a defined method of procedure. The term moisture simply means the loss in weight under fixed conditions of treatment. It is intended and does bring the material to a condition which can be duplicated closely and represents a fixed basis for comparison, but in no wise stands for all the water in the coal. The volatile combustible, as has been carefully investigated by Professor Parr, is by no means properly named. Only a fraction, and a variable fraction at that, depending largely on the kind of coal, is combustible, and a considerable fraction, consisting of water vapor, carbon dioxide, nitrogen and other diluents is inert or non-combustible. It is well to recollect that the proximate analysis of coal was devised many years ago, and primarily as a means of testing the amount of coke left by coal. The volatile combustible has since been the subject of much discussion and many attempts have been made to correlate it with heating value, geological changes and the various questions arising in coal utilization. Some undoubted connections have been shown, but I feel that possibly too little recognition has been given to the empirical and more or less uncertain nature of the determination.

Of growing importance, particularly in connection with coal washing, and as a means for the study of coal samples, is the application of the separation by gravity or the so-called "float and sink" tests, in which the coal crushed to a moderate degree of fineness is separated on solutions of high specific gravity, chloride of calcium for specific gravities up to 1.35 and chloride of sulphate of zinc for higher specific gravities. Chloride of zinc solution can be made of a specific gravity as high as 2 and by dilution any of the intermediate gravities can be obtained. I have used this method in my laboratory for years to separate heavy mineral materials like slate and pyrites, as preliminary to the study of the composition of coal. The method is excellently adapted to tracing out the variations in composition as the intermixed mineral substances are eliminated. It will enable the experimenter to distinguish with considerable accuracy between the inherent intimately mixed ash and sulphur compounds and the coarser and mechanical contaminations.

In recent years the leading factor in the commercial valuation of coals has become the calorific value or heating power of the coal and to-day the most important demand on the laboratory is the determination of this. The widely extending use of the bomb calorimeter is leading to new problems for the investigation of the chemists. Here again the heating value of the sample is modified more than by mere dilution by the nature of the mineral aggregate. As Mr. Turner and others have shown, the heating value is not entirely proportional in a given kind of coal to the residue left after deducting the ash and the moisture, but that there are factors depending on the influence of the inorganic material. Work of this kind is of great importance in order that the effect of ash, moisture and pyrites on the commercial value of coals may be more accurately known.

Calorimetry demands considerable training and experimental skill and the recently adopted policy of the Bureau of Standards of furnishing materials of known heating value so that the constants and correction of the calorimeter can be determined is greatly to be commended. The possibility of error in calorimetric determinations due to alteration of samples should be borne in mind. A very finely pulverized coal sample will oxidize in many cases very rapidly, and comparative results by different chemists on such a sample are liable to be very unsatisfactory unless all made at approximately the same time on samples that have been sealed in air-tight receptacles. Experiments made by the Fuel Testing Plant afford ample evidence of the extent to which this alteration may take place.

The determination of the water equivalent of the calorimeter experimentally gives rise to many difficulties and hence, except for those having had a great deal of experience in fundamental measurements, it is far better to use the calorimeter as a comparative instrument and depend for its constants upon burning substances of known calorific value such as are furnished by the Bureau of Standards. Commercial chemicals are quite variable and different samples of naphthalene, benzoic acid, etc., from different dealers will differ notably in their heating value. Recently the writer has obtained very successful results by the method of mixtures, adding hot water to the calorimeter from the Dewar flask or thermos bottle in which it is possible to read with great accuracy the temperature of the added water and to add the water to the calorimeter with only a very small correction for radiation loss during the addition. The method has proved successful in the hands of students who have made a number of water equivalent determinations agreeing within a very small limit of error with the calibration of the calorimeter obtained in other ways. Of course, this method has the advantage of being absolute and not relative.

The foregoing outline has dealt with the laboratory side of the question. All the analytical work, calorimetric work and everything else in connection with the testing depends for its economic value on the fundamentally representative nature of the sample of coal tested in the laboratory. Here is the weakest point in the commercial application of the results. Coal sampling is a matter now prominent before the technical world. Now that the extending

recognition of the value of laboratory work is leading to the purchase of coal on chemical specifications the whole question of sampling is under review. Ingredients most affected by sampling are obviously moisture, ash, sulphur, and calorific value. In a recent paper of great interest Mr. E. G. Bailey has presented a large number of results in which he criticizes existing methods and lays down certain general deductions from carefully conducted experiments as to the general principles involved in the securing of correct samples. Mr. Bailey has, in my opinion, done a very valuable piece of work both in calling attention to the importance of the subject and in the experiments that he has brought forward. As having been connected with the government work at St. Louis, I feel called upon to correct certain misapprehensions in regard to that work which I think have unintentionally on his part led him to place in a somewhat false light as to the accuracy with which the sampling was done. As I follow his paper he makes a fundamental assumption that the variations in the portions of coal taken at the plant from the same car shipment and sent to the Boiler, the Gas Producer and Briquetting and Washing Plants were identical in composition with the car load samples and that the variations shown in these different portions were due to variations in sampling of the portions at the various plants, whereas, the facts of the case are that the different portions taken from the car were not supposed to be sampled from the car but simply portions unloaded at different points, and the reason why analyses were made of the separate portions was because it was recognized that the car load was not uniform as far as contents of ash, sulphur, etc., were concerned, and that the car load analysis could not be taken for the different portions without a preliminary thorough mixing of the whole car load, which was not practical. This is clearly stated on page 284 of Professional Paper 48, Part 1, from which I quote:

> It was intended that the car sample should represent the average of the whole car, while the other samples stood for different portions of it. These would average about 5 tons each. In some cases the car sample was taken on only a part of a car. The large variation in the different samples in a few cases shows the irregularity in the coal in the car.

Experiments were made at St. Louis and published in this same work, giving the analysis of duplicate samples, and while the results were not very satisfactory and some errors were found, they were not of the magnitude given by Mr. Bailey from his comparison of the other samples based on the assumption which I have shown was not warranted and which was contrary to the facts as we stated them at the time. Br. Burrows has discussed the question of mine samples, but the comparison of these with coal shipped from the mines makes no allowance for the extent of cleaning that the coal underwent in shipping and in taking the mine samples. As stated, several duplicate samples on the car loads were run to check the St. Louis sampling and the worst result obtained, I think, was the one given on page 287, in which an extreme variation in ash on a coal averaging 15 per cent. ash was a little over 2 per cent. This coal was selected as the worst obtainable from the standpoint of sampling and the variation of the highest and lowest samples from the average of all the experimental samples on this coal was only a little over one per cent. Notwithstanding this criticism that I felt compelled to make of Mr. Bailey's representation of the St. Louis work, I feel that this general proposition in regard to the uncertain nature of much coal sampling is well sustained. His conclusion as to the amount of sample necessary in order to obtain a representative sample are of great interest. However, I do not feel that the difficulties are quite as great as his experiments would lead one to conclude.

Two things are important to consider:

In the first place, that in crushing coal a large proportion of fine material is produced so that the average size of particle is but little more than one-half the maximum size and therefore results on the distribution of the maximum size pieces greatly aggregate the difficulties. I recently took four samples of screened coal and had them put through a jaw crusher and screened.

In No. 1, 8.8 per cent. was retained by a 1/2″ screen and 56.4 per cent. passed a 1/4″ screen. This sample of coal was sampled in duplicate at this state of crushing, portions of coal of about five pounds being taken. The two five-pound portions were each separately pulverized, well mixed and analyzed. The first portion gave 13.86 per cent. ash and the second portion 13.56 per cent. A similar experiment on a second sample of coal gave 16.3 over a 1/2 inch screen and 46.65 per cent. through a 1/4 inch screen. The ash in the first sample, 14.59; in the second sample, 14.49. A third sample of coal gave 7.3 per cent. over a 1/2 inch screen and 48.3 per cent. through a 1/4 inch screen. The ash in the first sample was 15.11; in the second sample, 15.10. In two of these samples the percentage of ash in the finer portion was considerably greater than the percentage of ash in the coarser portion.

Of course, these results are too few in number to amount to anything, but they show that the finer material is in sufficient proportion to diminish the irregularity introduced by the bad distribution of the coarser lumps in the sample.

A further point in coal sampling which has to be considered is that in the larger sizes there is a natural mixture in the material of the slate and the coal, so that 4-inch lump coal does not represent a mixture of 4-inch lumps of coal and 4-inch lumps of slate to any appreciable percentage of the ash present. In other words, the inspection element must enter coal sampling, and no man would draw a moderate sized sample of a coal in which he has a large percentage of lumps of slate as large as the lumps of coal, while the occasional presence of even a large lump of slate would have but little influence on the ash percentage of the resulting sample.

Mr. Bailey gives what he names the size weight ratio or the relation between the maximum sized piece of coal in the sample and the weight of coal necessary to take in order that the sample may be certainly representative within an error of one per cent. of ash.

Now his figures lead to very large samples in cases of lump coal, but the foregoing indicates that the size ratio should probably be that of the maximum slate sizes present in the coal lumps, or free, rather than the actual coal lump size. The moderate variations in the ash percentage of the different lumps would have far less influence in disturbing sampling than the presence of equivalent sized lumps of slate.

Obviously, therefore, careful inspection must precede the sampling in the case of lump coal and the presence of large pieces of slate and pyrites in lumps in the coal taken into

consideration in determining the size of sample necessary in order to properly sample the coal.

I have always directed samplers to inspect the coal carefully and break up into small pieces any lumps of slate, bone coal or pyrites found or anything else that did not look like coal before taking or dividing the sample.

Of course, it is well known that no system of sampling which is purely mechanical is satisfactory for materials in which coarse distribution of the components exists, unless the whole of the material is crushed to approximately such limits as are defined by Mr. Bailey. This is the principle involved in the sampling of lead and copper, and gold and silver ores, where the system of sampling involves the crushing of many tons of material. Such a system of sampling is, of course, out of the question with lump coals where the crushed material would be to a certain extent rendered of small value. The system of sampling adopted in this case must be based upon an estimate of the maximum size of slate and pyrites, constituting an important portion of the impurities.

The difficulty of eliminating the personal element in doing such sampling is one of the problems which the Committee on Specifications will have to contend with. Meanwhile, the sampling problem is before us and must be adequately solved before the laboratory analysis of the coal reaches its full application.

The preparation of the laboratory sample from the field sample is a much more simple matter and is easily within the reach of present methods. One of the principal difficulties involved at this point is the avoiding of changes in the composition of the sample due to loss of moisture and to oxidation. I notice in many experiments the coal is ground to 100-mesh or even 200 before analysis. I think this is a step in the wrong direction. The finer the powder the more prone to oxidation and loss of moisture, and I think the effort of the sampler should be to determine a lower limit for Mr. Bailey's "size-weight-ratio" as well as a higher, and not to reduce the sample beyond this point, before weighing out for analysis.

We have considered that a sixty-mesh sample will meet the ordinary requirements where 1 gram is taken for the determination, which is within Mr. Bailey's figures as I understand them.

REVIEW.

PHARMACEUTICAL CHEMISTRY DURING 1908.

(*Concluded from page 260.*)

Organo-Therapeutics or Organo Remedials.

The first to call attention to this class of remedials was Brown Séquard, who advanced the hypothesis that "all glands of the body give to the blood useful principles, the absence of which is felt when these glands are extirpated or destroyed by disease." This hypothesis was extended to include various organs and that in a diseased condition of an organ, an extract prepared from the same organ of a healthy animal serves as a remedial agent. The efficacy of extracts of certain organs may be best judged by the success attending the use of such preparations as Iodothyrin (thyroid ext.), suprarenal preparations, testaden, spermin (testacle ext.), ovaraden (ovaries ext.), manimae (udder ext.), Linadin (spleen ext.), etc. New in this line are:

Manimin, an extract of the manimary glands, useful as hemostatic in uterine hemorrhage.

Paratoxin, a toxin obtained from bile and used in tuberculosis.

Leciferrin, a lecithin iron preparation from egg yolk.

Neuroprin, an extract of the nerve tissues useful in nervous diseases and as an antidote in strychnine poisoning.

Pancrobilin, a nucleo enzyme from the pancreas and gall, useful in constipation.

Orchicithin, an extract of the testes of the ox which is employed in sexual neurasthenia.

Astauxin, a calcium paranucleinate used as antirachitic.

Cellasin, a carbohydrate and fat splitting-ferment claimed to hydrolyze 3000 times its weight of starch or sugar.

Alkaloids and Glucosides.

Among the purin derivatives, Theophyllin (Theocin), a 1.3-dimethyl, 2.6-dioxypurin and its alkali double salts, still maintains a front rank among the diuretics. Through interaction between theobromin and monochlorhydrin, a dioxypropyl-theobromin has been prepared (Bayer, D. R. P. 191106). In an analogous manner, a 1.3-dimethyl-7-oxyethylxanthin has been prepared from theophyllin and glycolhydrin. Paraxan, a dimethylamino derivative of 1.7-dimethylxanthin, introduced by Boehringer and Sohn, has been withdrawn because of its irritant gastric action. Schwabe[1] has prepared various alkyl derivatives (ethyl, propyl, benzyl) of theophyllin and through oxidation of ethyl theophyllin, he obtained a dimethylparabehenic acid. These products are still in the experimental stage. A new diuretic is the double salt of theobromin sodium and sodium lactate called Theolactin.[2]

Morphine Derivatives.

The hydroxyl groups present in morphine are intimately associated with its toxic action, which, through its narcotic characters, differs from all other opium alkaloids, its action being chiefly upon the nerve centers of the brain. Upon closing these OH groups by substituting one or both of these hydrogens by alkyl or acidyl radicals, the narcotic characters disappear, while on the other hand, a spinal excitant (tetanic action) is developed. Thus, codeine produces, like morphine (but in lesser degree) narcosis, followed by an elevated reflex, which, if the dose be sufficiently large, develops tetanic convulsions. This action upon the spinal cord increases with the number and molecular weight of the alkyl groups introduced; hence codethylene, with its ethyl group, is more intense in action than codeine, which contains but one methyl group. Among all possible derivatives, it is immaterial as to whether an acidyl or alkyl radical, aliphatic or aromatic, is introduced. There is practically no qualitative difference in action so long as the same hydrogen is replaced. During recent years a number of derivatives of the codeine type have been introduced. These substances, while less active for relieving pain, exert a sedative effect on the unstriped muscles of the bronchi, and reduce the disposition to cough; hence are of value in phthisis, bronchitis, asthma, etc. Among these were Dionine, the hydrochlorid of ethyl morphine ($HO.C_{17}H_{17}.NO.OC_2H_5$,

[1] *Ber. d. chem. Ges.*, **40**, 1744.
[2] *Chem. Ztg.*, **1908**, 367.

HCl), Heroin, the hydrochlorid of diacetic ester of morphine, $(CH_3COO)_2C_{17}H_{17}ON,HCl$, and Epiosin, an amidazole derivative of morphigenine. Quite recently, the J. D. Riedel Co. has prepared a bromomethyl morphine derivative, morphosan (D. R. P. 166362, 175796, 191088), and the Knoll Co., a triacetyl derivative (D. R. P. 175068), the two hydrogens of the hydroxyls and one of the nucleus being substituted by acetyl groups.

Nascein: This opium alkaloid is employed to a limited extent as well an antispasmin (narcein sodium, sodium salicylate) and narcyl (ethyl narcein hydrochlorid) as sedatives and antispasmodics. Recently, the Knoll Co. have prepared various alkyl derivatives through action of dimethyl and ethyl sulphate on the alkali salts of narcein and homo-narcein (D. R. P. 174,380, 183,589). Esters of these are prepared through treatment with dehydrating agents as acid anhydrids, the carboxyl hydroxyl group with the H of the methylene, separate as water, yielding aponarceine (D. R. P. 187,138). Arecolin, the methyl ester of arecaidin, a myotic alkaloid found in the betel-nut, has been prepared synthetically by Wohl[1] from methylamido-β-dipropionic aldehydtetraethylacetal, by action of conc. hydrochloric acid, the resulting n-methyl-Δ-tetrahydropyridin aldehyd is through its oxim converted into methylhexahydronicotinic acid (arecaidin). Gadamer and Ginzel[2] find in columbo root, three alkaloids, analogous to berberin but differing in the number of hydroxyl groups and ester arts. Columbarim, $(C_{20}H_{22}NO_5)$, the principal alkaloid, contains 4 methoxy groups. New among the quinine salts are the nucleinate, a combination of 60% of the alkaloid and 40% of nucleinic acid, employed subcutaneously in syphilis and quinine anhydromethylenecitrodisalicylate, a compound of this alkaloid and novaspinin. This contains less quinine and more salicylic acid than a salicylate or the acetyl salicylate. Xaxaquin is a quinine acetyl salicylate which combines antirheumatic and analgesic effects. A new method for preparing esters of quinine is embraced in the German patents 178,172 and 178,173, of the Vereinigten Chinin Fabriken zu Frankfurt, utilizing the Grignard's reaction in which anhydrous quinine and alkyl, aryl or aralkyl magnesium halids react in presence of ether. The resulting quinine oxymagnesium halids are then esterified by acid chlorids or their anhydrids. Barger and Carr[3] propose the formula $C_{35}H_{39}O_5N_5$ for ergotin, the anhydrid of the amorphous ergotoxin (m. p. 162–164°), which is more active than the former.

Cannabinol: This active principle of hascheesh is assigned the formula $C_{21}H_{30}O_2$, boils at 230° (0.1 mm.), forms a yellow thick mass which oxidizes readily in the air. It contains a phenolhydroxyl and an aldehyd group.[4] Pictet[5] isolated pyrrolidin (C_4H_9N) and N-methyl pyrrolin (C_5H_9N) from tobacco. In poppy leaves, pyrrolidin and the base $C_{11}H_{18}N_2$ (b. p. 240–250°), called Dauien, similar to nicotin, were also isolated. In the seeds of the poppy, pepper, parsley and cocoa leaves, c-methylpyrrolin and other bases of the pyrrol series were isolated. The author considers that these simple bases, whose molecules contain hydrated pyrrol nuclei, are decomposition products of the albuminoid bodies of plants, from which, through condensation, high molecular complex alkaloids are formed. According to the work of Nierenstein[1] the Decker's formula for tannin, a derivative of phthalic anhydrid, is more probable than the older view of its digallic acid origin.

C. Liebermann[2] finds an oily base (b. p. 132–137° at 11 mm.) in cocaine, which is the ethyl ester of anhydroecgonin. Saxuranin is a glucosid $(C_{22}H_{24}O_{10})$ isolated from Prunus Pseudocerasus, m. p. 210–212°. Taxicatin is a glucosid of the Taxus baccata, which forms needles fusing at 166–167°. Velledol is the active constituent of Viscum album used in arteriosclerosis.

Miscellaneous Chemicals.

Phenyl dihydroquinazolin tannate has been introduced under the title of desalgin (A. Voswinkel, Berlin) as an appetizer. Plejopyrin is a condensation-product of benzamid and phenyldimethylpyrazolin (m. p. 75°), used in migrain. Quietol produced by the action of valeric acid on the product of the interaction between dimethylamin, chloroxyisobutyric acid and propyl alcohol, $(CH_3).(CH_2.N(CH_3)_2)$: $CO.CO.CH_2.CH(CH_3)_2.(COOC_3H_7)$, the substance fuses at 118° and is proposed as a sedative. Asiphyl is the mercury salt of p-anilinarsenic acid, possesses the combined action of atoxyl and mercury. Torulin, a dry stable yeast proposed in infectious diseases. Meligrin is a condensation product of dimethyloxyquinine and methylphenylacetamid used in migraine.

Thiozin is a linalyl sulphur compound used in all cases where sulphur is indicated for external use. Chromium sulphate has recently been recommended in locomotor ataxia, cirrhosis of the female breast, neurasthenia, functional impotency. Diacellulose is a hemicellulose preparation made from agar-agar through the action of enzymes or hydrolytic agents, used in diabetes.

Medicinal quackery existed in the earliest periods of history, whether practised by the Babylonians in placing their sick in the market places where the general public might prescribe, or as carried on by the Egyptian priests in the form of magic rites or as during the middle ages when it reached its zenith in the magic Theriacs, compounded mixtures of everything medicinal known, for which most extravagant claims were made. Such conditions continued until the complete separation of medicine and pharmacy which was made by legal status in Germany in 1350. During the period following, the apothecary took up manufacturing processes necessary for the preparation of all of his medicinal chemicals. This era was marked by the discovery of benzoic, lactic, hydrocyanic, citric, tartaric, tannic and pyrogallic acids, glycerol, ethyl acetate and nitrite, ether, morphine and the cinchona alkaloids. Most of these, as well as others not mentioned, were discovered by apothecaries. With the establishment of the firms of Schering, Merck, Riedel and others during the early part of the last century, competition and convenience transferred the art of manufacturing gradually from the apothecary to the manufacturing chemist. With the discoveries of chloral, chloroform, phenol, salicylic acid, etc., and the introduction of the patent system, the era of synthetic chemistry became firmly established. The accidental discovery of the anti-

[1] *Ber. d. chem. Ges.*, **40**, 4712.
[2] *Archiv. d. Phar.*, **244**, 255.
[3] *Jour. Chem. Soc.*, **91**, 337.
[4] *Czerkis Ph. Post*, 49.
[5] *Chem. Ztg.*, **1907**, 804.

[1] *Ber. d. chem. Ges.*, **40**, 916.
Ph. Jour., **641**, 3604.

pyritic properties of acetanilid in 1888 opened to synthetic chemistry an entirely new field, the application of pharmacology to structural organic chemistry. Since this, organic synthesis has achieved triumphs in all departments of materia medica, covering the fields of hypnotics, antipyretics, local anesthetics, antiseptics, diuretics, arsenicals, etc. The study of the structure of such natural products as morphine, cocaine, quinine, adrenalin, etc., has enabled the synthetic chemist to supply us with a large number of remedies, cheaper and in many respects superior to nature's originals. Within the last ten years, new conditions have arisen, which through the combined influences of quackery and competition, have not only thrown discredit on the true and legitimate fields, but also through superiority of numbers threatened their very existence. In various parts of our country so-called "Chemical Companies" have been established by certain promoters, whose past history will not bear close scrutiny, the objects of such companies being to flood the market with cheap imitations of well-established synthetics employing for this purpose mixtures in which acetanilid plays the part of the ingredient. Since this chemical possesses antipyretic, analgesic and antiseptic properties, the field of substitution is large. Such practices are not only culpable but criminal, in that they endanger the life of the patient, defeat the purposes of the physician, and place the standard products substituted in discredit. Standard synthetic preparations have also to contend with another evil, and this is the flooding of the market with certain low-grade chemicals of Swiss origin, which are sold under titles that leave no doubt as to the purpose for which they are intended. Such imitations of standard medicinal synthetics which have attained standing in the medical profession are to be had through these channels at prices far below the legitimate cost of production.

Still another class of so-called synthetics have appeared, which practically flood the market and destroy confidence in the legitimate aims of true synthetic chemistry in the interests of pharmacology and medicine. This is the abuse and application of the term "synthetic" as applied to simple mechanical mixtures. Such preparations are given titles either similar in character to our true synthetics or such as would indicate their use; these are then variously described as "condensation" or "reduction-products," produced by secret processes upon a mixture of a number of well-known medicinal chemicals, securing thereby a "shot-gun" combination of them all. The following will illustrate:

Nephaldol: According to the manufacturers, this is prepared through the action of citric and salicylic acids on phenetidin in certain proportions, and after the reaction is over the resulting free acids are neutralized by quinine and sodium carbonate. Examination of this preparation has shown it to consist of a mixture of sodium salicylate, phenacetin and quinine.

Arseniol: This is given the simple title of sodiumchlorophosphoricoarsenate and is sold at $9.00 a pound. Analysis has demonstrated it to consist of a mixture of sodium arsenate, phosphate and chlorid.

Nopain, lauded as a synthetic, consists of a solution of cocaine, phenol, adrenalin and glycerol in alcohol.

Many other citations might be made, but this suffices to illustrate the deception practised upon the medical profession, who, of course, are unable to distinguish the true from the false. Certain classes of physicians are not blameless for this condition of affairs, as the following notice will show. Recently a journal devoted to the exposure of business frauds, "Der seelle Geschaeftsmann" of Cologne, has inserted in a reputable journal the following notice:

"For Physician. Wanted: Licensed physicians who are disposed to furnish favorable reports for advertising purposes of a newly introduced chemical preparation of epochmaking importance (germicide). Fee from 500 to 1000 marks."

As a result, a large number of offers from physicians were received in reply. One among these ran as follows: He was owner of a well-patronized dispensary in a large city and was not forced to earn tainted money. He was, however, prepared to give the desired opinion and thought it best for the manufacturer to furnish him with the report already prepared, as the manufacturer was the best judge of what was needed.

Further comments are unnecessary. V. COBLENTZ.

NOTES AND CORRESPONDENCE.

THE NEW BRADY GAS FILTER.

Owing to the installation of gas engines for blast furnace gas in the largest iron and steel works throughout the country, the chemists of these various plants have been confronted with several problems in gas analysis. One of the most difficult of these to solve satisfactorily was the determination of dust in gas.

Before blast furnace gas can be used in gas engines it must be subjected to a thorough cleansing. This is usually accomplished in three steps: dry cleaners, wet cleaners and final mechanical scrubbers. When ready for the gas engine the gas must contain only about 0.005 of a grain of dust per cu. ft.

The fine physical condition of the dust in the engine gas (gas ready for engine), and the large amount of dust and moisture in the raw gas make the accurate determination of dust per cu. ft., in either case, no easy matter. It was after trying all the forms of apparatus now known for such determination, with little success, that the Brady Gas Filter was devised.

This apparatus consists of four parts as shown, disconnected, in Fig. 1. Part 1 (numbered from left to right) consists of a brass shell provided with an outlet and an inlet. Part 2, the filter, consisting of an ordinary 94 mm. by 33 mm. Soxhlet extraction shell, is supported within Part 1. The brass shell is of such diameter that there is a space of about 3/16 of an inch between the paper shell and the inner surface of the brass shell. The method of supporting the filtering shell within Part 1 is by securing the edge of the former between two correspondingly tapering cylindrical faces. One of these faces is within the inlet end of Part 1, and the other is on the outside of a brass cylinder, Part 3. These tapering faces form a wedge which securely holds the paper cartridge in place, acting as its own washer, and protecting a space of about 1/2 inch inside the opening of the filter paper from dust, so that it can be handled with safety after the experiment. Part 3 forms the extreme inlet of the apparatus, and is provided with inside threads so that

it can be screwed to a sampling pipe. Its inner surface must be perfectly smooth so that there is no chance for accumulations of dust before the filter is reached. Part 4 is a loose nut which holds Parts 1 and 3 together while in use.

The apparatus may be used in any position but the preferred arrangement is horizontal. When the gas to be filtered contains moisture the filtering device must be heated to about 100° C. by enclosing it in an asbestos-lined box, heated with an electric light, or by any other available means. The nipple on the exit end of Part 1 is provided with threads so that it can be removed and replaced with aluminium tubes, containing a dehydrating agent, in case it is desired to determine moisture in the gas (see Fig. 2).

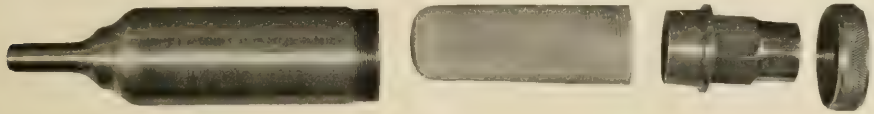


Fig. 1.

The advantages of this apparatus as to simplicity are easily seen. Gravity seems to cause the heavy particles of dust to settle on the bottom of the shell, while the lighter particles form a porous coating on the upper surface. This action prevents the filter paper from becoming clogged as long as heat enough is applied to keep the paper dry. About twice as large samples of gas can be passed through this apparatus as through any other we have ever tried. We have also found the number of grains of dust per cu. ft. to be higher when determined by this apparatus than with the others.

Fig. 2.

Thus far the device has been used for filtering blast furnace gas only, but there is no reason why it cannot be used to filter air or any other gas. The apparatus described is now being made and sold by E. H. Sargent & Co., whom I desire to thank for the loan of that shown in the illustrations.

L. A. Touzalin.

Laboratory of Illinois Steel Co.,
So. Chicago, Ill.

[From the Department of Plant and Animal Chemistry, Massachusetts Agricultural Experiment Station.]

VOLUMETRIC DETERMINATION OF COPPER IN SUGAR ANALYSIS.[1]

The co-operation of the laboratory in the experiments conducted by other departments of the Station has often rendered necessary quantitative determinations of reducing sugar, sucrose, lactose and starch in a variety of products. The final step in every case is the determination of the cuprous oxide precipitated from Allihn's solution by the reducing action of the sugar. After a rather long study of different methods of filtration and the various ways of determining the amount of precipitate as copper, cuprous and cupric oxides, the following method was adopted since it proved the most satisfactory and yielded the best of results if reasonable attention was paid to details. It might be said, further, that as such work often has to be done at odd times it is desirable to maintain a supply of sugar tubes[1] and only to titrate when there are a number of tests on hand. By exercising a little care the same tubes can be used repeatedly without change of felt.

The process consists of heating an aliquot of the sugar solution with the mixed Allihn's solution (30 cc. of "white," 30 cc. of "blue" and 60 cc. of water) and filtering by aid of suction through a sugar tube with an asbestos felt supported by glass wool. The cuprous precipitate is transferred to the tube, washed with hot water until free from alkali and then with alcohol. The copper is dissolved in 5 cc. of concentrated nitric acid, thoroughly washed with hot water, and the filtrate run into an Erlenmeyer flask by means of suction. The solution is evaporated to small volume or, at least, until nitrous fumes are no longer given off. Too great concentrations should be avoided as it often results in the precipitation of a very insoluble form of copper and the loss of the determination. Twenty cc. of a saturated solution of zinc acetate, 20 cc. of potassium iodide (165 g. to 1000 cc.) and 60 cc. of water are added and the free iodine titrated with N/10 sodium thiosulfate solution (24.83 g. per liter). The thiosulfate is run in gradually, with constant shaking, until the brownish yellow color (iodine) has been largely destroyed, then 2 cc. of starch paste (1 g. to 200 cc.) are added and the titration continued until the blue particles have entirely disappeared. Towards the end of the reaction the flask should be stoppered and shaken thoroughly.

The copper equivalent of the thiosulfate is determined by diluting 25 cc. of a standard copper solution with water, evaporating and titrating exactly as in the test. The standard solution is prepared by dissolving 10 grams of pure dry metallic copper in 200 cc. of concentrated nitric acid and making up to a liter with water at 20° C. The solution should be analyzed gravimetrically and will keep almost indefinitely. From this data the reducing action of the sugar solution can be readily calculated in terms of copper and by conversion tables the corresponding amount of sugar. While the first reading of this method might give the impression that it was rather difficult, in reality after a few trials it is extremely simple, can be carried out rapidly and the titration is very sensitive.

E. B. Holland.

[1] An adaptation of the Low zinc-acetate method.

[1] Eimer and Amend, No. 3263.

MERCURY SEALS IN FAT EXTRACTION APPARATUS, AND A NEW FORM OF FLASK.

One of the first to mention and describe a mercury seal in connection with chemical apparatus is Karsten[1] who used it in gas analysis apparatus to prevent the gases from coming in contact with corks or rubber stoppers or tubing. Fig. 1 shows his arrangement and needs no further explanation. Michaelis[2] was the next to describe a mercury seal, shown in Fig. 2; it is all glass and was used for making horizontal connection between the parts of the apparatus where cork or rubber would be objectionable. Schwartz[3] describes and illustrates an apparatus to be used for extraction with ether, ligroin, etc., in which he used two mercury seals for

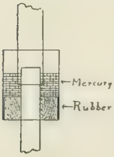


Fig. 1.

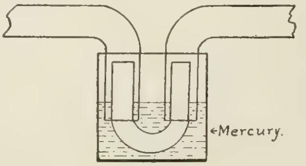


Fig. 2.

connecting the different parts of his apparatus; his method is shown in Fig. 3, the parts being all glass. Until this time nobody had used a mercury seal for connecting a fat extraction flask with a condenser. Knorr[4] was the first to describe such an arrangement; his flask is shown in Fig. 4, while Fig. 5 shows his condenser with a thimbel, *A*, fused on at its lower end; *B* is an extraction tube with a perforated platinum disk fused in near the bottom for holding the substance to be extracted. For extracting a finely divided substance some kind of packing not affected by the solvent must be put on this disk. The thimble *A* (Fig. 5) fits over

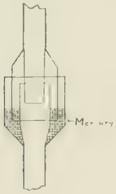


Fig. 3.

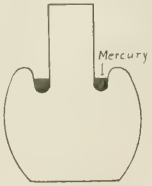


Fig. 4.

the neck of the Knorr flask (Fig. 4) and dips into the mercury contained in a channel around the neck. Near the lower end of the extraction tube there are three short nipples which rest on the neck of the flask, while the tip extends into the flask. In this original form the Knorr apparatus is in use in many laboratories to-day and is listed in all catalogs of chemical apparatus. The flask of this apparatus, however, has a serious disadvantage: on account of its shape it is extremely hard to clean or to transfer anything from it. The first attempt to overcome these difficulties was by Wheeler and Hartwell,[5] who used a flask of the usual

[1] *Zeit. anal. Chem.*, **11**, 213.

[2] *Dingl Polyt. Journ.*, **247**, 36.

[3] *Zeit. anal. Chem.*, **23**, 368.

[4] Proc. 7th An. Con. Assoc. Off. Agr. Chem., 1890 (*Bull.* **28**, Bur. Chem.).

[5] *Journ. Am. Chem. Soc.*, **23**, 338.

shape with a grooved rubber stopper around its neck as shown in Fig. 6. The use of rubber in contact with glass which is heated is, however, never very satisfactory, and especially in this case since the flask must be cleaned for weighing. To make the apparatus more rigid, Robison[1] used a collar made of maple wood, fitted tightly to the neck of the flask by means of a perforated rubber stopper as shown in Fig. 7, using a flask as shown in Fig. 6. This combination is in use in several large laboratories. The small size of flask in this combination, as well as its shape, makes it somewhat difficult to clean, although a great improvement over the original Knorr shape. An improved form of flask is described by DuBois[2] and is shown in Fig. 7, being of the usual Erlenmeyer shape, which, in connection with a shorter

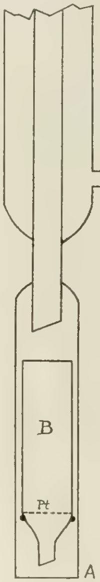


Fig. 5.

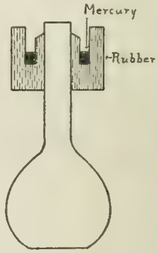


Fig. 6.

and wider neck, is easily cleaned; this flask was used with the wood-collar rubber stopper combination for holding the mercury. After using this latter arrangement for some time one will become convinced that rubber should not be used in contact with heated glass; also that some care is necessary in order to make the joint mercury tight. To overcome the difficulties mentioned in the various forms and arrangements, all of which the writer has used, a flask shown

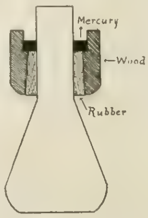


Fig. 7.

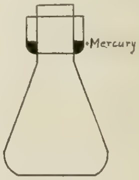


Fig. 8.

in Fig. 8 was made for the writer by a New York firm. It is all glass, Erlenmeyer shape, large neck, can be easily cleaned and substances transferred from it without difficulty; it fits the usual Knorr condenser. It has now been in use

[1] Private communication.

[2] *Journ. Am. Chem. Soc.*, **30**, 797.

for one year and has shown no defects. About the same time when this flask was being made, a flask almost identical in form was imported from Germany; it is, however, a much heavier and taller flask with a smaller neck, but fits the Knorr condenser and is a much more serviceable flask than those in which rubber is used.

ALBERT P. SY.

BUFFALO LABORATORY,
BUR. CHEM.,
U. S. DEPT. AGRICULTURE.

VARIATION OF MOISTURE CONTENT IN BUTTER AS SHOWN BY DIFFERENT METHODS OF SAMPLING.

The desirability of adhering to fixed methods of analysis is acknowledged by practically all analytical chemists. Of course, it is understood that deviations must be resorted to, to meet conditions which are not identical in different laboratories, but aside from minor changes in methods, it is recognized as unwise, especially in official work, to make a marked change in the fixed and essential details of any method, unless such change has been sanctioned by collaborative work by different analysts.

Even now, it appears that some chemists do not pay sufficient attention to the details of sampling, apparently losing sight of the fact that inaccuracies in sampling at the beginning of an analysis nullify the effects of most careful work later on.

Some time ago the writer had occasion to investigate the effect of different methods of sampling of butter by official inspectors, and the results are so striking that they are given here for publication.

The butter sampled was contained in sixty-pound tubs, and the method followed was an exact duplicate of the method followed by the official inspectors.

First Experiment.—Sample No. 1. Taken with butter ladle from the edge of the bottom of the tub, approximately one pound being taken.

Sample No. 2. Taken with ladle from the center of the bottom of the same tub.

Sample No. 3. Regular official method of sampling with butter trier, five plugs drawn diagonally from the whole length of the tub.

Water, No. 1, 12.82–12.80%. Average, 12.81%.
Water, No. 2, 13.35–13.29%. Average, 13.32%.
Water, No. 3, 12.00–12.19%. Average, 12.09%.

Second Experiment.—No. 1-*a*. One-pound sample taken with ladle from center on top of sixty-pound tub.

No. 2-*a*. One-pound sample taken with ladle from center on bottom of same sixty-pound tub as in 1-*a*.

No. 3-*a*. One-pound sample taken with ladle from edge of bottom of same sixty-pound tub as in 1-*a*.

No. 4-*a*. Sample taken with butter trier in regular official way, five plugs being withdrawn diagonally from the length of the tub.

Water, No. 1-*a*, 13.87–13.80%. Average, 13.84%.
Water, No. 2-*a*, 14.43–14.52%. Average, 14.48%.
Water, No. 3-*a*, 14.77–14.69%. Average, 14.73%.
Water, No. 4-*a*, 14.12–14.04%. Average, 14.08%.

Third Experiment.—No. 1-*b*. Sample taken with ladle from edge of bottom of sixty-pound tub.

No. 2-*b*. Sample taken with ladle from center of top of same sixty-pound tub as 1-*b*.

No. 3-*b*. Sample taken with ladle from center of bottom of same sixty-pound tub as 1-*b*.

No. 4-*b*. Sample taken with trier from two sections of the tub and split lengthwise with a knife; no regular official sample taken in this case.

Water, No. 1-*b*, 14.33%.
Water, No. 2-*b*, 13.62%.
Water, No. 3-*b*, 15.57%.
Water, No. 4-*b*, 13.40%.

Fourth Experiment.—No. 1-*c*. Sample taken from sixty-pound tub by inverting tube, removing same, rejecting a layer one and one-half inches thick from the bottom and securing the sample, approximately one pound, from the center of the butter remaining.

No. 2-*c*. Sample taken in regular official way from the same tub as 1-*c*, the butter trier being used, securing the sample diagonally from the whole length of the tub.

Water, No. 1-*c*, 20.5%.
Water, No. 2-*c*, 17.6%.

From the above it will be seen that different methods of sampling the butter are responsible in these cases for a variation as high as 2.9%. Indeed, there appears no reason why there should not be even greater variation than above when the manner in which water is held in butter is considered. A variation of 2.9% is sufficient to account for a flagrant violation of the 16% water limit of the Internal Revenue Department, and official inspectors and chemists should view with much concern the method of sampling of the product before final judgment is passed.

The exceeding great desirability, therefore, of adhering to the tried methods of sampling is in these experiments decidedly emphasized.

As to effects of prolonged drying on moisture determination in butter, I have found that by the official method four to five hours is the limit beyond which variation in moisture is no greater than the difference between parallel determinations.

FLOYD W. ROBISON.

LABORATORY, MICHIGAN DAIRY
AND FOOD DEPARTMENT.

EXTRACTIVES FROM GAYAULE (PARTHENIUM ARGENTATUM).

This is a record of work done with gayaule, plant and rubber, in January, 1906.

The samples as received comprised a stalk of gayaule about two feet high, about a pound of the comminuted plant resembling coarse sawdust, and a small sample of the rubber produced commercially by mechanical means.

A microscopic section of the stalk was made for me by Dr. Norman Mason, of this city. The making of the section was said by Dr. Mason to be a difficult matter, the wood being about as hard as a cherry stone and the bark soft, and dragging on the knife on account of the rubber, oils and resins contained in the latter.

Iodine green was found to stain the rubber cells. These cells were entirely in the bark. There was none of the root to the sample.

The rasped wood, a factory product, was divided into 15 gm. portions. On one of these the moisture determination was made by keeping in a vacuum over sulphuric acid for 48 hours at room temperature.

This method was adopted as there were other volatile

matters not water present in the sample. The moisture found was 4.5 per cent.

Another portion was burned for ash, and yielded 3.56 per cent. Of the ash 61.0 per cent. was calcium carbonate.

Another 15 gm. portion was extracted with acetone in a Soxhlet extractor. The product, after evaporating the acetone and drying at 105°, amounted to 9.57 per cent. This product was saponified with alcoholic potash. On separating the saponifiable from the unsaponifiable, the fatty and resin acids amounted to 3 per cent. of the weight of the wood. The unsaponifiable was 2.2 per cent. of the wood.

The discrepancy between the 9.57 per cent. taken and the 5.2 per cent. recovered was due in part to the fact that part of the original extract was water-soluble and another part volatile.

No effort was made to separate the various fatty and resin acids.

The 2.2 per cent. of unsaponified matter was somewhat interesting. It had a buttery consistency and when warmed an odor suggesting at once menthol and oil of rose geranium.

On the same portion which had been extracted by acetone and after drying the same, an extraction was made with benzol. From the benzol extract the "rubber" was precipitated with a large quantity of alcohol. After drying, this product weighed 5.04 per cent. This should not be taken as the total rubber in the sample, for unless the cell walls are ruptured it is not to be supposed that the rubber solution can pass out.

On another original portion the boiling water extract dried at 105° weighed 6.1 per cent. This extract was entirely soluble in warm water to a yellow solution. The solution did not precipitate gelatin, gave but a slight precipitate with ferric alum and possessed no dyeing properties. The odor was that of logwood extract.

This ended the work on the wood. A portion of the gayaule rubber as produced by mechanical means was dissolved in benzol and the rubber precipitated by alcohol. The yield was something like 45 per cent.; I have mislaid the figures.

It is undoubtedly the presence of a large quantity of resinous matter associated with the rubber that enables the extractives to collect together as the wood is ground under water. The ground wood floats off and the rubber gradually collects as one mass under the roller.

Is there not a hint in this for the collection of the rubber contents of the milkweed? The rubber from the latter is of far finer quality than the gayaule product, which would hardly be used were it not for the high price of the real rubbers of commerce.

CHAS. E. SWETT.

PROVIDENCE, R. I., April 9, 1909.

Editor Journal of Industrial and Engineering Chemistry.

DEAR SIR: In the April number of the *Journal of Industrial and Engineering Chemistry*, page 280, is a report of a judicial decision concerning Adeps Lanae and Wool Grease or "Degras."

While the particular decision is manifestly correct, the report contains a quotation from a previous judicial decision which describes wool grease. This description is radically wrong. Wool grease does not contain "from 15 to 20 per cent. of potash." It contains no potash. Of course I am now referring to the commercial product and not the wool fat or suint as occurring in the wool.

The writer has seen this decision brought up by the examiners where it was relied on to tax wool grease of somewhat different appearance from the ordinary, under a higher classification.

In the cases mentioned the appraisers were not sustained, but the curious thing is that a description so easily proven wrong should be so frequently quoted.

Yours truly,

CHAS. E. SWETT.

MR. BAILEY'S PAPER ON ACCURACY IN SAMPLING COAL.[1]

This paper is the most important contribution to the question of paper sampling that has appeared for years. It is deserving of the highest praise, and though our experience is not in accord with all the conclusions reached by the author, particularly conclusion No. 1 in the summary, in which he states that errors from 3 to 5 per cent. in ash determinations are of ordinary occurrence, and errors of from 15 to 30 per cent. are frequently encountered, still we recognize its great value.

Assuming that every delivery of coal to the plant we have in mind, contains the same percentage of ash, the variations from the average ash of many hundred determinations ranged from 2 per cent. below to 3 per cent. above this average. But as the coal is not entirely uniform in composition, as shown, first, by inspection, and secondly, by the boiler house records where the amount of coal and resultant ash is regularly weighed, and the amount of combustible remaining in the ash determined, and the power developed from the coal recorded in terms of electrical units per pound of coal, we must conclude that the real error is probably much less than the maximum error indicated above.

These figures are obtained from a plant where the coal as unloaded is run through a crusher, and the crushed coal is sampled by taking a scoop at regular intervals, a representative of the coal company being present during the sampling, though the actual work is done without his aid. The sample drawn as indicated above is broken down by hand and quartered in the ordinary way, the sample received at the laboratory filling a Mason's fruit jar of one quart capacity. This sample represents about 400 tons. The general results of this method are entirely satisfactory to the parties concerned, as indicated by the fact that this mode of sampling has been in use for more than ten years at this plant, and there is always active competitive bidding by the coal companies for the business.

The specifications are rather severe, and heavy fines are exacted for failure to meet the requirements, nor is a premium allowed for coal that surpasses the standard set in the contract.

Taking up the more frequent cases where a purchaser receives but one car in each shipment, and the money settlement for this coal is made upon the findings of the chemist, and where the necessities of the case require a sampling of the car before receipt by the purchaser, hence before unloading there are two points which must be considered and

[1] See THIS JOURNAL for March.

duly weighed: first, the amount of money that can be profitably expended in drawing and testing samples, and secondly, the accuracy in sampling that is attainable without prohibitive cost.

The difference in value between good semi-bituminous coal of from 5 to 7 per cent. ash and poor coal with 12 to 15 per cent. ash, in this market is 30 cents per ton, so that the whole possible difference between the buyer and the seller is $15.00 per car. The cost of sampling by this method outlined below may be put at $1.50, so that there remains $13.30 for "over-head" charges, which must include chemists' charges, transportation of samples, profit to consumer or coal merchant. It can thus be seen that the sampling cost must be kept low in order that there be some advantage occurring to the parties concerned. The sampling method which we have used for fifteen years is as follows: Three holes are dug in the coal, one in the middle of the car, the other two at diagonal corners of the car. Large scoops full of coal are taken every 12 to 15 inches on the way down, care being exercised to get a fair proportion of lump and fine coal. This gross sample is broken down by hand, quartered and sampled in the ordinary way. To carry out this sampling requires from three to four hours' time of two properly trained laborers.

Using the method as outlined, our experience is that on successive samplings of the same car, the first being made by ordinary laborers trained for it, and the second, when the samples are drawn under our personal supervision, both yield results upon analysis differing by less than 1 per cent. in ash, which means a difference in price, upon the specifications, commonly in use here, of from $3.00 to $4.50 per car. This possible difference of $4.50 per car, when the total difference involved is only $15.00, would be an unsurmountable obstacle to the laboratory valuation of single cars of coal, were it not for the fact that in practice the analysis of the single car represents simply one of a number of shipments, and the error is evidently not always in the same direction.

We commend Mr. Bailey's paper for putting in concrete and clear form the errors that must arise from imperfect sampling, and the precautions that must be taken to secure any desired degree of accuracy. He evidently realizes that the most important applications of his work will be to sampling materials other than coal, where the value of the cargo is many times that of coal, and where errors admissible in coal work would mean a large monetary loss to one of the parties concerned. We have had an opportunity to judge the practical accuracy of "car sampling" of coal at a plant where the power developed from the fuel is used to pump water, and the efficiency of the coal is measured in "feet pounds" per pound of fuel. The variations in the composition as shown by the analysis are accompanied by corresponding variations in the work done at the plant. At this plant coal containing over 10 per cent. ash is rejected, so that the variations studied only comprises a total difference of 5 per cent. in ash.

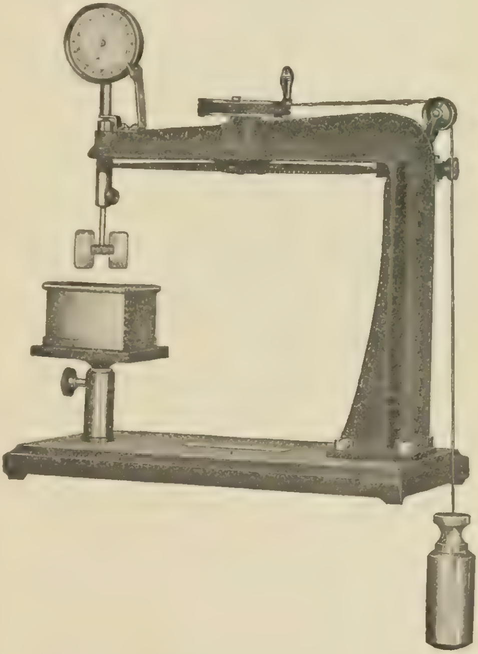
The exposition of the relation between the analytical and the mathematical results in Mr. Bailey's paper is extremely good, and we consider the points he makes in regard to drawing a large gross sample, and the initial reduction of this gross sample to a sufficient degree of fineness, to be distinct and important contributions. We have also realized the importance of this, but never has it been put before us in such a logical and convincing form.

As we have said before, Mr. Bailey's paper has a greater value for the proper sampling of materials other than coal; and we wish to congratulate the author upon the admirable selection of the substance used to demonstrate his points, as he could hardly have found any material other than coal upon which accurate analytical data could have been so easily obtained. In fact the paper should have a more comprehensive title.

PENNIMAN & BROWN.

A NEW VISCOSIMETER.

We are in receipt of the particulars regarding the new Stormer Viscosimeter, designed by Chief Chemist Stormer, of the J. I. Case Threshing Machine Co., and made by the Bausch & Lomb Optical Co., Rochester, N. Y. The instrument is distinctly new in design, and since it comes from a practical chemist who has found it superior to other forms in making a large number of determinations daily, it may be expected to appeal to other practical men.



The principle employed is that of a paddle wheel driven by a constant force. This paddle wheel is equipped with indicator so that the number of revolutions made in a liquid within a given time may be recorded, or the time required to register a given number of revolutions may be used as the basis for determining the comparative viscosities of oils, varnishes, etc. The principal points of advantage which have been gained are:

Only a 50 cc. sample is required for the determination of viscosity and the temperature of this small quantity may be easily controlled.

Only a few seconds are required to make a test and the temperature variation during the test is negligible.

The reading may be repeated and checked with great ease, it being only necessary to wind the indicator back to zero in order to be ready to repeat the determinations.

The force exerted is constant throughout the experiment.

Different oils may be run successively without the loss of time, since a clean cup and a cleaning of the small paddle wheels puts the instrument in order for a new test.

With this viscosimeter there is not such a great variation in viscosities as is shown in some of the outflowing types of instrument.

Only the stop-watch need be kept in mind, since the number of revolutions is automatically recorded and a convenient brake stops the revolutions of the wheel instantly at the desired moment.

Further information, directions for use, and prices may be obtained of the makers.

BOOK REVIEWS AND NOTICES.

Post's Chemish-Technische Analyse: Handbuch der analytischen Untersuchungen. Dritter Vermehrter and Verbesserter Auflage, Herausgegeben von Prof. Dr. Bernhard Neumann. 8vo., Bd. 1, pp. xxix, 974. Braunschweig: F. Vieweg und Sohn, 1906–'08. Price, M. 23.50.

The third edition has retained the arrangement of the second so far as possible, but much has been rewritten and much new matter has been added. The editor calls especial attention to the new matter under Calcium Carbide and Acetylene, Asphalt and Pitch, Cadmium, Aluminum, Chromium, Tungsten, Vanadium, Molybdenum, Hydrofluoric Acid, Bromine, Sodium Sulphide, Antichlor, Alumina and Aluminum Sulphate.

Like Lunge's book covering the same field, this was written by specialists and must therefore necessarily be somewhat uneven in merit. The actual value of such a book can scarcely be determined in any other way than by actual use and no estimate of it will be attempted. The printing and illustrations are of the high order that we have grown to expect from the firm publishing it. EDWARD HART.

The Chemistry of Essential Oils and Artificial Perfumes. By ERNEST J. PERRY. Second edition. Cloth, 8vo., viii + 546 pp. London: Scott, Greenwood & Son. New York: D. Van Nostrand Co., 1908. Price, $5.00 net.

Since 1899, when the first edition of this most excellent work by Mr. Perry appeared, it has served as a standard guide and reference book to all chemists and others who had to do with the examination of essential oils and artificial perfumes. There were 411 pages in the first edition and these have been increased to 546. Many parts of the book have been rewritten and brought down to date and much new matter has been added. One chapter which appeared in the first edition, namely, that on terpeneless oils, has been omitted inasmuch as, in the opinion of the author, this subject does not appear to be of sufficient importance for detailed treatment. Among the interesting chapters containing new matter are those on rosemary, lavender and spike-lavender, and linaloe oils. In this edition a comprehensive appendix in the form of three large insert sheets has been added, showing at a glance the standards laid down for the principal essential oils in eleven pharmacopoeias of the principal countries. In the second edition Mr. Perry's work will unquestionably continue to be a leading source of information and a standard work of reference to chemists everywhere. The typography and general make-up of the book are beyond criticism. W. D. RICHARDSON.

NEW BOOKS.

Die Entwicklung der Leuchtgaserzeugung seit 1890. By W. BERTELSMANN. Sammlung chemischer und chemisch-technische Vorträge. XII. Band, 7 und 8 Heft. 90 Ss. mit 38 Abbildungen. Stuttgart: Ferd. Enke, 1908. Preis, M. 2.40.

Die Lack-und Firnisfabrikation. In: Monographien über chemisch-technische Fabrikationsmethoden. By PROF. MAX BOTTLER. Verlag Wilhelm Knapp, Halle a/S, 1908. Preis, geh., M. 4.50.

Mine Sampling and Chemical Analysis of Coals Tested at the United States Fuel-testing Plant, Norfolk, Va., in 1907. By J. SHOBER BURROWS. Washington, D. C. (Office of the Superintendent of Documents), 1908 (1909). 23 pp., 8° (U. S. Geol. Survey, Bull.).

Die Analyse des Kautschuks, der Guttapercha, Balata und ihre Zusätze. By DR. RUDOLPH DITMAR. Verlag von A. Hartleben. Wien und Leipzig, 1908. Mit 42 Textabbildungen und 4 Tafl. Geheftet M. 11.

Decorative Glass Processes. By ARTHUR L. DUTHIE. New York: D. Van Nostrand Co., 1908 (1909). 278 pp., ill., 8°. Price, $2 net.

The Fractionation of Crude Petroleum by Capillary Diffusion. By M. P. CRAM and JOS. ELLIOT GILPIN. Under the Supervision of D. T. Day. Wash., D. C., Office Supt. of Documents, 1908 (1909). 33 pp., diagrs., 8°. (U. S. Geological Survey Bull.).

Die Untersuchung von Eisengallustinten. By F. W. HINRICHSEN. Stuttgart: Verlag Ferd. Enke, 1909. Preis, M. 4.40.

Kalzium cyanamid (Stickstoffkalk oder Kalstickstoff) als Düngemittel. By E. KEMPSKI und H. IMMENDORFF. Stuttgart: Eugen Ulmer. 124 Ss. Preis, geh., M. 3.50.

Alloys and Their Industrial Applications. By E. F. LAW. Philadelphia: Lippincott, 1909. 16 + 269 pp., ill., cl. Price, $4 net.

The Dyeing and Cleaning of Textile Fabrics. By F. A. OWEN. A Handbook for the Amateur and Professional. Based partly on notes of H. C. Standage. New York: John Wiley & Sons; London: Chapman and Hall, Ltd., 1909, 12° vi + 253 pp., cl. Price, $2.00 (8/6 net).

An Introduction to the Science of Radioactivity. C. W. RAFFETY. New York: Longmans, Green & Co., 1909. 14 + 62 pp., cl. Price, 75 cents net.

Die Grundzüge der allgemeinen Chemie und die Technik der Untersuchung der Rohmaterialien und der Betriebskontrolle in der Seifenindustrie. By DR. C. STIEPEL. Verlag für chemische Indüstrie, H. Ziolkowsky Ausburg.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN CHEMICAL SOCIETY.

Indianapolis Joint Meeting.

A very successful joint meeting of the Middle West Sections of the American Chemical Society was held on Friday and Saturday, March 26th and 27th, under the auspices of the Indiana Section at Indianapolis. The participating Sections were the Chicago, St. Louis, Cincinnati, Louisville, University of Illinois, Columbus and Indiana. The program was as follows:

FRIDAY, MARCH 26, 1909.

7.00 P.M.—Dinner at the German House, corner Michigan and New Jersey Streets. After dinner was served there were addresses as follows:

The American Chemical Society .... W. R. WHITNEY
Camphor .... W. A. NOYES
Address .... JOHN URI LLOYD
Address .... C. F. MABERY

SATURDAY, MARCH 27, 1909.

The Sections met in Shortridge High School, 3rd floor, north side, corner North and Pennsylvania Streets, at 9 o'clock. The following papers were presented:

A Method for Use in Volumetric Analysis (10 min.) .. .. W. R. SMITH
Some Analytical Methods Connected with the Examination of Boiler Water (15 min.) .... S. W. PARR
Urinary Nitrogen of Men in Health (20 min., Lantern) .. .. H. S. GRINDLEY
The Destruction of Platinum Crucibles through the Ignition of Magnesium Ammonium Phosphate (10 min.) .... R. E. LYONS
Research Work Being Carried on in the Ohio State University (20 min.) .... ——— ———
Fermentation with Respect to Fusel Oil Content (15 min.) .... A. M. BRECKLER
The Preparation of Hydroxamic Acid from Hydroxylamine Salts of Organic Acids (15 min.) .... R. OESPER
On the 3′,3′-Diketonic Acids (15 min.) ...... J. B. GARNER
Electro-Deposition of Metals from Perchlorate Baths (10 min.) .... F. C. MATHERS

The members of the Society were the guests of Pitman-Myers Co., pharmaceutical chemists, at an informal noon luncheon at their laboratory, 111–117 N. Capitol Avenue.

The afternoon was given to visits to Eli Lilly & Co., pharmaceutical chemists, 210–214 East McCarty St., and to Kingan & Co's packing house, Union Stock Yards.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Minutes of meeting called by the temporary committee to discuss advisability of holding the Eighth International Congress of Applied Chemistry in New York City, held at the Chemists' Club, on April 3, 1909.

W. H. Nichols in the chair.

After a few introductory remarks, in which he explained the proceedings up to date, the chairman, Dr. W. R. Nichols, opened the meeting.

The minutes of the previous meeting were read by the Secretary, and duly approved.

A great many letters were read, in which great interest in the movement to secure the meeting of the Eighth International Congress of Applied Chemistry in New York was expressed, and it was noted that not a single disapproval of the plan was received.

The report of the committee appointed to obtain congressional action was read, duly approved, and made a part of these minutes.

Votes of thanks were extended to the Hon. Burton Harrison, Congressman of New York, and to Dr. H. W. Wiley, on motion of Prof. Bogert, seconded by Prof. Baskerville, and the committee was discharged on motion of Dr. Charles A. Doremus, seconded by Dr. T. J. Parker.

Dr. Wiley, addressing the meeting, stated what progress had been made in preparing for the next (seventh) Congress of Applied Chemistry in London.

Mr. Toch moved that the invitation to the Eighth International Congress of Applied Chemistry to meet in New York, which is to be issued by the Government, should be supported by invitations from American universities, educational institutions, scientific associations and individual firms; that a circular should be sent by the Secretary requesting the issuance of these invitations and addressed to the Honorable General Secretary of the Seventh International Congress of Applied Chemistry, Mr. William Macnab, 10 Cromwell Crescent, London, S. W., England; that these invitations should be sent in care of the secretary of this committee prior to May 15th, so that all the invitations together can be handed to the congress authorities in London. This motion was seconded by Dr. Baekeland, and unanimously carried.

It was decided to leave the discussion of the financial side of the congress until after the invitation had been finally accepted.

It was also decided to continue the work with the temporary committee and leave the permanent organization until the invitation has been accepted.

The following universities, educational institutions, scientific organizations and industrial establishments were represented at the meeting:

Harvard University, by Clifford Richardson.
Columbia University, by M. T. Bogert.
Cornell University, by W. D. Bancroft.
University of Pennsylvania, by Walter T. Taggart.
University of Pittsburg, by W. A. Harmon.
Massachusetts Institute of Technology, by Henry Howard.
College of the City of New York, by Charles Baskerville.
Syracuse University, by E. N. Pattee.
Lafayette College, by Edward Hart.
New Hampshire College, by Charles L. Parsons.
Rutgers College, by R. G. Wright.
Polytechnic Institute of Brooklyn, by Irving W. Fay.
Massachusetts Agricultural College, by Chas. Wellington.
Chemists' Club of New York, by I. F. Stone.
Franklin Institute of Philadelphia, by S. P. Sadtler.
American Chemical Society, by C. L. Parsons, M. T. Bogert, T. J. Parker, Wm. McMurtrie, L. M. Dennis and A. P. Hallock.

American Electrochemical Society, by C. A. Doremus, E. F. Roeber and A. von Isakovics.

Society of Chemical Industry, by William H. Nichols.

American Institute of Chemical Engineers, by S. P Sadtler.

Verein Deutscher Chemiker, by A. P. Hallock.

N. Y. Section American Chemical Society, by L. H. Baekeland.

N. Y. Section Society of Chemical Industry, by M. Toch.

N. Y. Section American Electrochemical Society, by E. F. Roeber and G. A. Sperry.

N. Y. Section Verein Deutscher Chemiker, by E. G. Love.

New England Sec. Society of Chem. Industry, by Henry Howard, A. A. Claflin and L. Loring.

Lehigh Valley Section American Chemical Society, by E. Hart.

Philadelphia Sec. American Chemical Soc., by W. T Taggart, W. C. Cornell and C. E. Vanderkleed.

North Eastern Sec. American Chemical Soc., by Henry Howard and A. A. Claflin.

Manufacturing Chemists' Assn. of the U. S., by Henry Howard, chairman Executive Com.

General Chemical Co., by W. H. Nichols and T. J. Parker.

Grasselli Chemical Co., by Harry C. Grant.

Roessler & Hasslacher Chemical Co., by J. Hasslacher.

Arnold Print Works, by Roscoe L. Chase.

Cochrane Chemical Co., by L. Loring, Vice-Pres.

Niagara Electrochemical Co., by J. Hasslacher.

Merrimac Chemical Co., by H. Howard, Vice-Pres.

Carl H. Schultz (Inc.), by A. P. Hallock.

Schoelkopf, Hartford & Hanna Co., by I. F. Stone.

Toch Bros., by Maximilian Toch.

Nichols Copper Co., by W. H. Nichols.

Perth Amboy Chemical Works, by J. Hasslacher.

Badische Co., by Adolf Kuttroff.

Farbenfabriken of Elberfeld Co., by H. Schweitzer.

H. A. Metz & Co., by E. A. Widmann.

National Aniline & Chemical Co., by I. F. Stone.

Hudson River Aniline Color Works, by L. I. Waldman.

Institute of Fermentology, by M. Wallerstein.

Eimer & Amend, by F. Klein.

National Gum & Mica Co., by J. Alexander.

Charles Eneu Johnson & Co., by Chas. H. Spayd.

Charles Lenning & Co., Inc., by W. C. Cornell.

H. K. Mulford Co., by E. E. Vanderkleed.

Naval Smokeless Powder Works, by Geo. W. Patterson.

Adjourned.

H. SCHWEITZER,
Secretary.

NEW YORK, April 7, 1909.

DEAR SIR.

At the last meeting, held April 3rd, representatives of many American universities, educational institutions, scientific organizations and industrial establishments were present, all evincing the greatest interest in the plan of inviting the Eighth Congress of Applied Chemistry to meet in New York in the year 1912. A large number of letters were also received in which the movement was heartily endorsed, without a single expression of disapproval.

The meeting was informed that a joint resolution, "authorizing the President of the United States to invite the International Congress of Applied Chemistry to hold its eighth meeting in the United States of America, in the year Nineteen Hundred and Twelve," had been passed by the 60th Congress.

To supplement this official invitation on the part of our Government, it was decided to call upon American universities, educational institutions, scientific organizations and industrial establishments to request the Seventh Congress, which will be held in London during the week of May 27th to June 2nd, to accept this invitation. It was concluded that this would be best accomplished by special letters, promising every assistance to make the Eighth Congress an extraordinary success in this country.

You are, therefore, respectfully asked to address such a letter to the Honorary General Secretary, Mr. William Macnab, 10 Cromwell Crescent, London, S. W., England, and to send it prior to May 15th, in care of the undersigned secretary, who will take charge of such communications and deliver them as a whole to the authorities of the Seventh Congress.

Trusting that you will comply with this request, which will not place you under any financial obligation whatsoever, I am,

Yours very respectfully,

H. SCHWEITZER,
Hon. Secretary N. Y. Section, Society of Chemical Industry,
117 Hudson Street, New York City.

AMERICAN SOCIETY FOR TESTING MATERIALS.

Coal Specifications Committee.

The American Society for Testing Materials has appointed a large and representative Committee on Coal Specifications. The work of the committee will be to determine upon suitable specifications for the purchase of coal for different purposes, which will be satisfactory alike both to producers and consumers of coal. The organization of the committee embraces the appointment of various sub-committees to consider the various subdivisions of the subject. The work in the first instance will be done mainly by correspondence, the suggestions received from the different members being assembled by the sub-committees and then transmitted to the members of the sub-committees for further recommendations and advice. It is not anticipated that many meetings will be necessary. It is hoped that this most important work will be carried through at an early date to a successful and satisfactory conclusion.

PERSONAL NOTES.

Mr. G. M. MacNider was appointed, on Jan. 1st, Feed Chemist and Microscopist of the North Carolina Dept. of Agriculture. Mr. MacNider was formerly Assistant Chemist of Soils in the same Department.

Dr. W. A. Syme, Assistant Chemist to the N. C. Experiment Station, and Assistant Professor of Chemistry at the Agricultural and Mechanical College of the State, has been appointed State Oil Chemist.

Mr. Philip McG. Shuey, formerly chemist for the Savannah Guano Co., has opened a laboratory for fertilizer and fertilizing materials in Savannah, Ga.

The Fuel Testing Company, 220 Devonshire St., Boston,

has been organized for the purpose of assisting the consumer in the selection of fuel and the most economical operation of boiler plants and other heat generating systems, with Mr. E. G. Bailey as mechanical engineer and Mr. W. B. Calkins as chemist.

OFFICIAL REGULATIONS AND RULINGS.

FOOD INSPECTION DECISION 106.

Amendment to Food Inspection Decision 77 (A definition of the terms "Batch" and "Mixtures" as used therein).—The definition of the term "batch" as given on page 4, lines 12 to 14 of Food Inspection Decision 77, is hereby extended to include also the contents of any one package, cask, or other container holding 500 pounds or less of dye, even though the contents of such package, cask, or container has not undergone the same treatment at the same time and the same place as a unit.

The word "mixtures" as used on page 3, line 15 from the bottom, and following, of Food Inspection Decision 77, is hereby declared to mean not only such mixtures as consist wholly of certified coal tar dyes but also those which contain one or more certified coal tar dyes (and no other coal tar dyes or dye) in combination with other components, constituents, or ingredients not coal tar dyes, which other components, constituents or ingredients are in and of themselves or in the combination used harmless and not detrimental to health or are not prohibited for use in food products; the exact formula of such mixtures, including all of the components, constituents, or ingredients, or other parts of the mixture, together with a statement of the total weight of mixture so made, must be deposited with the Secretary of Agriculture and a one (1) pound sample thereof must be sent to the Secretary of Agriculture, but such formula need not appear on the label; in lieu of which may appear the legend "Made from certified lots Number ——— and Number ———, etc.," and no mention need be made of any constituent or constituents other than those of the certified coal tar dyes employed.

H. W. WILEY,
F. L. DUNLAP,
GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved:
JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., March 19, 1909.

JUDGMENTS, FOOD AND DRUGS ACT.

No. 38, February 17, Misbranding of Canned Corn (Underweight).

No. 43, March 13, Misbranding of Canned Peas (as to weight).

No. 44, March 13, Misbranding of Meal (as to milling process).

No. 45, March 13, Adulteration and Misbranding of Whiskey (as to color, age and source).

No. 46, March 13, Adulteration of Eggs (Filthy, decomposed animal substance).

No. 47, March 13, Misbranding of Maple Sirup (as to presence of maple sirup).

No. 48, March 17, Adulterated and Misbranded Vanilla Extract (a colored imitation).

No. 49, March 17, Misbranding of Coffee (as to geographical source).

(T. D. 29627—G. A. 6887). March 16, 1909. *Casein or Lactarene.*—The article commercially known as casein or lactarene *held* to be free of duty as lactarene, under paragraph 594, tariff act of 1897, and not at 20 per cent. *ad valorem* as a nonenumerated manufactured article under section 6 of said act.—United States *v.* Brownell (T. D. 29374) followed.

(T. D. 1446.)

Denatured Alcohol.

Authorizing Formula No. 1 for use in the manufacture of textile cleaning soaps and wall-paper removers.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., December 28, 1908.

SIR: You are hereby informed that Formula No. 1 (to 100 gallons of alcohol add 5 gallons of approved wood alcohol) is hereby authorized for use in the manufacture of textile cleansing soaps. You will please inform the ——— of this authorization, in compliance with their application forwarded in your letter of the 15th instant.

You are also informed that the same formula, No. 1, is hereby authorized for use in the manufacture of wall-paper removers. You will please inform the ——— of this authorization, in compliance with their application of the 8th instant.

Respectfully,
JOHN G. CAPERS, *Commissioner.*

MR. CHAS. W. ANDERSON, *Collector, Second District, New York.*

United States Circuit Court of Appeals, Sixth Circuit. No. 1809.

Hartman and Hartman *v.* United States.

Error to the circuit court of the United States for the northern district of Ohio.

(Decided February 2, 1909).

Before LURTON and SEVERENS, Circuit Judges, and KNAPPEN, District Judge.

LURTON, *Circuit Judge*, delivered the opinion of the court:

The plaintiffs in error were jointly indicted and convicted for violation of the act of August 2, 1886, as amended by the act of May 9, 1902, known as the oleomargarine act. The indictment contained eighteen counts. Count 1 charges a violation of Section 3 of the act by carrying on the business of manufacturers of oleomargarine without having paid the special tax required by law. Counts 2, 3, 4, and 5 charge violations of Section 13 of the act by failing to destroy stamps on emptied oleomargarine packages. Counts 6 to 14, inclusive, charge a violation of the thirteenth section of the act by refilling stamped packages which had contained tax-paid oleomargarine. Counts 15, 16, and 17 charge violations of Section 5 of the act by failing to keep books, give the required bond, and put up sign. Count 18 charges a violation of Section 17 by defrauding or attempting to defraud the United States of the tax on colored oleomargarine produced.

The defendant Henry Hartman was found guilty on all the counts. The defendant Frank Hartman was found guilty upon counts 6 to 14, inclusive, and not guilty upon the other counts. Each of the defendants was adjudged to pay a fine of $1,000 and to be imprisoned in the Cleveland workhouse for a period of six months.

A motion that the Government be compelled to elect upon which count it would proceed or demand a conviction was overruled. There was no reversible error in this. The offenses joined were merely statutory misdemeanors of the same class, and the fact that various penalties were attached by which imprisonment in a penitentiary was possible under some of the counts did not prevent a joiner of counts under Revised Statutes, 1024. Morris *v.* United States, 161 Fed. Rep., 672. Both defendants were found guilty under counts 6 to 14, inclusive. Those counts rest upon section 13 of the oleomargarine act, and charge the offense of packing oleomargarine in old stamp-paid packages which had been emptied and upon which the stamps had not been destroyed. The judgment awarded was one which might have been imposed under the general verdict upon these counts irrespective of any other. When there are a number of counts in an indictment and the verdict is a general one, a judgment which might have been awarded under any one of the counts will be applied, upon a writ of error, to any count good in law upon which there was evidence to go to the jury. The question was given full consideration in a similar case in which the opinion of this court has just been filed. Hardesty *et al. v.* United States. It follows, therefore, that we need consider only those counts upon which both defendants were convicted, namely, those from 6 to 14, inclusive.

Those counts were for refilling empty stamp-paid oleomargarine tubs or packages, the old stamps upon which not having been destroyed, contrary to the provision of the 13th section of the act which reads as follows:

"That whenever any stamped package containing oleomargarine is emptied, it shall be the duty of the person in whose hands the same is to destroy utterly the stamps thereon; and any person who wilfully neglects or refuses so to do shall for each such offense be fined not exceeding fifty dollars, and imprisoned not less than ten days nor more than six months. And any person who fraudulently gives away or accepts from another, or who sells, buys, or uses for packing oleomargarine, any such stamped package, shall for each such offense be fined not exceeding one hundred dollars, and be imprisoned not more than one year. Any revenue officer may destroy any emptied oleomargarine package upon which the stamp-paid tax is found."

There was evidence tending to show that the plaintiffs in error were engaged in the business of manufacturing oleomargarine by mixing with the white, tax-paid oleomargarine a coloring material which gave the product the yellow shade of butter for the purpose of selling, vending, or disposing of the same to persons other than those of their own family tables and that they had packed this colored produce so made by them in tubs, baskets, or packages which had contained tax-paid colored oleomargarine and had been emptied and that they had done this fraudulently, knowing that the stamps upon the said emptied packages had not been destroyed as required by law when the packages were emptied.

By far the most important of the evidence resulted from a search of the premises occupied by the plaintiffs in error and in which they carried on their business. The evidence thus disclosed was objected to as incompetent upon the theory that the search warrant under which it had been procured was irregular and illegal. We need not stop to determine the regularity of the search warrant, for, conceding it to have been illegally issued or illegally executed, the evidence which was thereby discovered was not incompetent under the direct authority of Adams *v.* New York (192 U. S., 585) and Hardesty *et al. v.* United States, decided by this court (164 Fed. Rep., 420).

Aside from the errors assigned upon admissibility of evidence already briefly noticed, the assignments go the charge of the court. It is difficult to know the precise objection upon which counsel rely. We have given attention to the parts excepted to and to the charge as a whole. We find no error of which plaintiffs in error can complain.

Judgment affirmed.

(T. D. 29636). *Drawback on Alloy.*

TREASURY DEPARTMENT, March 20, 1909.

SIR: The Department's regulations of April 16, 1901 (T. D. 22963), providing for the allowance of drawback on Babbitt metal manufactured by Merchant & Co. (Incorporated), of Philadelphia, Pa., with the use of imported lead and antimony, are hereby extended, so far as applicable, to cover the exportation of alloy manufactured by the Leddell-Bigelow Company, of New York City, in part from imported lead, antimony, and antimonial lead, in accordance with the sworn statement, dated February 20, 1909, transmitted herewith for filing in your office.

In liquidation, the quantities of imported lead and antimony and antimonial lead which may be taken as the bases for the allowance of drawback may equal the quantities declared in the drawback entry, after official verification of exported quantities, provided they shall not exceed 87-1/2 pounds of lead and 12-1/2 pounds of antimony for each 100 pounds of alloy exported, with an allowance for waste not to exceed 1 per cent. of such quantities.

Respectfully,

JAMES B. REYNOLDS,
(63422.) *Assistant Secretary.*

COLLECTOR OF CUSTOMS, NEW YORK.

(T. D. 29651). *Carnauba-wax Substitute.*

UNITED STATES *v.* MORNINGSTAR.

U. S. Circuit Court of Appeals, Second Circuit. March 16, 1909. No. 185 (suit 4964).

1. MINERAL WAX—POPULAR MEANING.

There being no mineral waxes in a chemical sense, the provision for "wax * * * mineral" in paragraph 695, tariff act of 1897, must have been used according to the popular meaning of those words.

2. CARNAUBA-WAX SUBSTITUTE.

Carnauba-wax substitute, which is compounded of carnauba wax (a vegetable wax) and paraffin (a mineral wax) and is to all appearances a waxy substance used for the same purpose as other waxes, is free of duty under paragraph 695, tariff act of 1897, relating to "wax, vegetable or mineral."

3. CONSTRUCTION—SYNTHETIC CLASSIFICATION—ARTICLE COMPOUNDED OF TWO ENUMERATED SUBSTANCES.

An article compounded of two enumerated substances may be classified under a provision separately enumerating those substances; as carnauba-wax substitute, which, being composed of a vegetable and mineral wax, is classifiable under a provision for "wax, vegetable or mineral."

APPEAL from the Circuit Court of the United States for the Southern District of New York.

[Decision adverse to the Government.]

The decision below (T. D. 29121) affirmed a decision by the Board of United States General Appraisers, G. A. 6609 (T. D. 28220), which had reversed the decision by the collector of customs at the port of New York on merchandise imported by Charles Morningstar & Co.

J. Osgood Nichols, assistant United States attorney, for the United States.

Everit Brown, for the importers.

Before LACOMBE, COXE, and NOYES, Circuit Judges.

This cause comes here upon appeal from a decision of the Circuit Court, Southern District of New York, affirming a decision of the Board of General Appraisers, which reversed a decision of the collector, classifying the merchandise in suit as a nonenumerated manufacture under the provisions of the tariff act of 1897.

Per CURIAM: The relevant paragraphs are both on the free list and read as follows:

PAR. 695. Wax, vegetable or mineral.

PAR. 633. Paraffin.

The importation is known as "carnauba-wax substitute," carnauba wax being a vegetable wax. The Government's chemist admits that, although the so-called mineral waxes are not regarded as waxes in the chemical sense, paraffin belongs to that group. Evidently Congress used the words "mineral wax" in their popular sense, otherwise they would cover nothing. The article in question is compounded of carnauba wax and paraffin, and when completed is to all appearances a waxy substance used for the same purpose as are other waxes and containing no animal wax. We concur with the Board and the Circuit Court.

The decision is affirmed.

(T. D. 1472). *Oleomargarine.*—The placing of bottles or other containers of coloring matter in original packages of oleomargarine by manufacturers is not warranted by the law and regulations, and goods found on the market in such condition will be subject to seizure.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
WASHINGTON, D. C., March 23, 1909.

To Collectors, Revenue Agents, and Others Concerned:

Recent investigations of violations of the oleomargarine law, through the addition of coloring matter to the uncolored product by keepers of hotels, restaurants, and boarding-houses, developed the fact that some manufacturers were sending out original packages of oleomargarine with bottles or capsules of coloring matter placed therein, and this practice leads the purchasers to believe that it is sanctioned by the Government and they have a right to thus manipulate the goods.

Section 6, act of August 2, 1886, as amended, prescribes the manner of packing oleomargarine by manufacturers and retail dealers, it being specifically provided that the goods shall be packed by the manufacturers in firkins, tubs, or other wooden packages, marked, stamped, and branded as the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, shall prescribe, and no authority is given in this section for the placing of extraneous matter in these packages.

Section 20 of this act provides:

That the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, may make all needful regulations for the carrying into effect of this Act.

Under this section the Commissioner is empowered to make "all needful regulations" for the execution of this law, and in view of the violations growing out of the practice on the part of manufacturers of shipping original packages with bottles, tins, capsules, or other containers having therein coloring matter, packed within such original packages, it is clearly within the power conferred upon the Commissioner by Section 20 to prohibit by regulations this practice, especially as there is no provision in the law to warrant it.

It is held, therefore, that the placing by manufacturers in original packages of oleomargarine bottles or any other form of containers of coloring matter is not warranted by the law and regulations, and must be discontinued. Officers of this Bureau are instructed to warn manufacturers against this practice and to inform them that the continuance of the same after receipt of this notification will subject the goods found on the market to seizure.

JOHN G. CAPERS,
Commissioner.

INDUSTRIAL AND TRADE NOTES.

Phosphate Imports of Germany.

Supplementing the report of one year ago by the Berlin consulate-general on the sale of phosphates for fertilizers in Germany, Consul-General Robert P. Skinner now sends additional information from Hamburg:

The use of superphosphates by German farmers is practically universal. There is also a great and growing demand for a crushed furnace-slag fertilizer consisting of 14 to 18 per cent. phosphoric acid and 40 per cent. of lime,[1] concerning which I may make future communication, as it is a material of great utility in softening soils, and one which the United States could produce, probably, in unlimited quantities. The German phosphate-rock importers desire 77-degree rock, with a tolerance of 1 degree, but they have been getting American shipments of as low degree as 73 degrees. All prices are quoted per degree and per ton. The present price is about 8.5 d. ($0.17) per degree.

The world's total production of phosphate rock increased in 1907 to the amount of approximately 250,000 tons. The United States produced about 135,000 tons less than in the previous year, Algeria and Tunis about 320,000 tons more, and the South Sea Archipelago about 43,000 tons more. The progressive production of phosphate in northern Africa is to a great extent a consequence of the increasing demand on the part of European agriculture, which has almost absorbed the entire quantity produced.

[1] Thomas slag —Ed.

In the course of 1907 the first shipments of phosphate from Nauru, German Polynesia, appeared on the local market. The quality is good, and this product is considered a valuable addition to the several kinds of phosphates imported from the Polynesian Islands. Owing to the improvements made on the island of Nauru, both in respect to mining and shipping facilities, it is expected that larger quantities of Nauru phosphate will be imported.

Phosphate, which is free of duty when imported into Germany, is ground and converted into superphosphate, by treatment with sulphuric acid, in numerous factories in this country. It requires about $30,000 to erect a factory to produce 3,000 tons of such acid.

The demand for phosphate, generally, is growing, but this is not the case as respects Tennessee rock. As the following statistics show, the exports of Tennessee phosphate have decreased. Hamburg and the adjoining city of Harburg import chiefly Florida rock phosphate and the Algerian product. Considerable quantities are also received from Tunis.

Of the shipments of phosphate arriving in Hamburg very small quantities are re-exported, the chief consumers being the German farmers. It would not be remunerative for the German superphosphate factories to seek a market for their article outside of Germany, in northern Europe, or elsewhere, as well-organized competing factories may be found wherever there is any considerable demand for this fertilizer.

While the freight rate per ton of phosphate from Algerian ports is 7 s. ($1.70) per ton, and from Tunisian ports 7 s, 6 d. ($1.82), shipments from American ports are generally subject to a freight rate approximating 10 s. ($2.43). Of late almost no ships have arrived here from ports in the United States carrying whole cargos of phosphate. This article now usually arrives in lots of 1,500 to 2,000 tons, on tramp steamers loaded with other bulk goods, such as cotton, cotton seed, cereals, etc.

The statistical situation of phosphate rock is as follows:

Exports from American Ports.

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	474,053	490,366	572,311	561,040	591,719
Florida pebble.	315,612	364,446	404,985	482,912	564,702
Peace River, Fla.........	62,910	81,650	91,155	41,742	36,729
Tennessee	113,948	121,965	94,301	101,466	92,112
So. Carolina...	67,445	90,000	78,802	.....	.....
Total.......	1,033,968	1,148,427	1,241,554	1,187,160	1,285,262

American Exports to Europe.

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	469,597	483,559	546,944	550,521	584,799
Florida pebble	141,251	219,166	218,838	209,617	296,371
Tennessee....	113,948	121,965	80,298	88,105	92,172
Total	724,796	824,690	846,080	848,243	973,342

German Imports from United States.

	1903	1904.	1905.	1906.	1907.
Florida rock..	304,935	284,780	261,407	314,820	278,226
Florida pebble.	20,250	71,700	30,582	24,770	50,189
Total......	325,185	356,480	291,989	339,590	325,415

Exports from Algeria and Tunis.

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Algeria.......	301,112	344,969	347,747	302,262	343,087
Tunis.........	360,621	457,133	529,645	757,993	1,040,300
Total.......	661,733	802,102	877,392	1,060,255	1,383,387

Imports at Hamburg and Harburg.

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	120,669	105,493	138,795	146,676	140,504
Florida pebble.	.....	.....	....	.....	19,632
Algeria.......	21,326	29,125	40,415	40,430	36,675
Gafsa.........	22,330	8,525	6,250	10,600	11,091
Senam........	.....	.....	....	3,000	1,500
Ocean Island..	2,700	4,800	5,450	7,300	.....
Christmas Island........	3,772	5,950	2,788	3,000	2,950
Aruba........	750	3,150	1,227	2,808	.....
Total......	171,547	157,043	194,925	215,814	212,352

The total production of all countries was as follows:

	1906. Tons.	1907. Tons.
United States	2,052,000	1,917,000
Tunis......	758,000	1,040,300
Algeria	302,300	343,000
South Sea Islands	247,000	290,000
France..................	469,400	476,700
Belgium.................	163,600	180,000
Other countries...........	100,000	100,000
Total..................	4,092,300	4,347,000

The quotations at end of December, 1907, in Hamburg, per degree per 1,000 kilos (2,204.6 pounds), were:

	Per cent.	Cents.
Florida hard rock	76 to 80	17.1 to 18.6
Florida pebble...........	68 to 73	13.6 to 14.0
Tennessee...............	78 to 80	15.7 to 16.2
Algeria	63 to 70	14.3 to 14.8
Algeria (Tunis)..........	57 to 63	13.6 to 14.0
Tunis-Gafsa	57 to 63	14.0
Christmas Island.........	80 to 85	20.7
Ocean Island and Nauru..	83 to 87	20.7

U. S. Consular Report, March 30, 1909.

Formosa Camphor Exports.

The following review of the Formosa camphor trade is by Consul Carl F. Deichman, of Tamsui:

The total amount of camphor exported in 1908 shows a decrease of over 1,000,000 pounds from the previous year, and is attributed to the increased activity in the camphor districts of China and Japan, and especially to the extensive use of synthetic camphor in various arts and manufactures in which formerly the natural camphor was used. This decrease was steady, notwithstanding the fact that the price of the natural product fell considerably.

The demand has slightly increased with the present year, 1909, but it is not likely that the amount exported will total the amounts exported in previous years from this island. The following table shows the export of camphor from Formosa during the year 1908, with the countries to which exported and the quantity and value to each in pounds and United States gold:

Countries.	Pounds.	Value.
United States	1,365,910	$ 524,100
England	458,850	166,681
France	277,970	100,460
Germany	53,200	19,522
Hongkong	560,196	241,936
British India	3,990	1,419
Japan	535,591	250,102
Total	3,255,507	$1,304,220

More Patents Revoked in United Kingdom.

Consul-General Robert J. Wynne, of London, reports that, on the ground that the articles are not sufficiently manufactured in the United Kingdom, the following patents have keen revoked:

The British-Westinghouse Electric and Manufacturing Company (Limited) have a patent for an arc lamp, but grant a license to a German company to export the lamps to Britain. The British comptroller-general held that there was no evidence to prove that the German company could not manufacture this article in the United Kingdom and sell at a profit at present prices.

Another revocation was of a patent to United States patentees, for fastening strips used in box-making.

Essential Oils in Sicily.

In answer to inquiries, Consul William Henry Bishop, of Palermo, furnishes the following information concerning essential oils in his district and the effects of the earthquake on the industry in Sicily:

No bergamots are grown in Sicily, and no bergamot oil is produced in this consular district. The whole supply has been coming from a small section of southern Calabria, opposite Messina, one of the regions most afflicted by the disastrous earthquake of December 28 last. The great production of essential oils, including orange oil, has been at Messina and vicinity, and 75 per cent. of the total production for Italy was customarily exported from that place. Our late consul at Messina, Dr. Arthur S. Cheney, had made a report on the subject, which no doubt covered the conditions, practically for all of Sicily, up to that time. (Published in Consular Trade Reports for January 23, 1909.)

The average annual production of orange oil in the Province of Palermo has been about 1,100 pounds. None is manufactured in the provinces of Trapani, Girgenti, and Caltanissetta, constituting the remainder of the consular district. Even the output of this vicinity was usually sent to Messina for export. The season of manufacture begins with September and ends with December, or in the more elevated region may be prolonged through January. There was seen in 1908 the phenomenon of low prices with a small output, while prices in 1907 were high with a very large output. This was due to the fact that, owing to the profitable rates then realized, there had been a great rush to produce, resulting in large stocks being left over.

The result of the earthquake has been to double or triple prices of essential oils. This large advance is true of all derivatives of the citrus fruit, such as citrate of lime, citric acid, etc. It is believed, however, that the panic of alarm from the disaster is being used to some extent as an element of speculation. A considerable stock was really found in the warehouses unharmed by the general destruction of Messina; factories remain in the small towns near there, such as Ali and Barcellona, and, as the time demanded for manufacture is not long, fruit which would under ordinary circumstances have been exported, will be rapidly made up into essences, etc., to meet the demand. Prices may therefore be soon expected to drop much nearer to a normal level.

It was one of the signs of awakening life at Messina that two manufactories of citrate of lime were opened at Gazzi, a suburb of that city, before January 20th. Some ten thousand families in the province of Messina and Catania, engaged in the industries following the harvesting of the citrus fruits, were thrown out of employment by the earthquake.—*U. S. Consular Report*, March 20, 1909.

Artificial Silk Manufacture.

The following report concerning the manufacture of artificial silk in France, and its relative merit as compared with silk manufactured from the so-called "natural fiber," is furnished by Consul John C. Covert, of Lyons:

The following information on the subject of artificial silk is a translation of a communication received from a prominent French manufacturer in answer to a number of interrogatories which I had submitted to him:

There are three varieties of artificial silk, to wit: Chardonnet, or nitrocellulose; Givet, or cuproammoniacal; and Xanthate cellulose, or viscose. There are five great mills and a number of smaller ones in France in which these three methods are employed. The smaller mills have not succeeded on account of the heavy expenses compared to the small product. The large mills are the Chardonnet, at Besançon, which produces from 1,763 to 2,204 pounds per day; the Givet process, at Givet, in the Vosges, which produces 1,763 pounds per day—this company has a smaller factory at Izieux, Loire, which turns out about 440 pounds per day of silk hair (crin)—and the Viscose Company, at Arques-la-Bataille (Seine-Inferieure), which produces 1,763 pounds per day, and which is expected in two months to have a capacity of 2,645 pounds—this company has another Viscose mill at Vals, which produces 440 pounds per day and will soon turn out 771 pounds per day.

There is no important manufacture of artificial silk in the United States, although that country consumes about 882,000 pounds per year. Machinery enters very largely into the cost of the production of viscose, and as machinery is brought to a high state of perfection in the United States I cannot see why the high rates of wages should prevent the successful manufacture of viscose in that country.

The Givet is an improvement on the Chardonnet process and the Viscose is an improvement on the Givet. It may be roughly stated, considering the quantity of production, consumption, freight, and wear and tear of machinery, that the cost of production is $2.70 to $2.90 per kilo (2.2 pounds) for the Chardonnet, $2.30 to $2.50 for the Givet, and under $2 for Viscose.

The Viscose method embodies as far as appearance, qual-

ity, touch, and cheapness are concerned, all the finest and best qualities. Instead of employing the expensive raw material, such as cotton, at 20 cents per 2.2 pounds, ordinary wood pulp is used at 5 cents per 2.2 pounds. Instead of using expensive dissolvents, such as alcohol or ether, ordinary water is sufficient.

You ask if we have succeeded in making an article which is not damaged by dampness or water. This talk about damages by water is a prejudice, for there is no tissue made where artificial material solely is employed, if we expect the tresses and gallons, elastic tissues which are especially made at St. Chamond and Barmen, but these are combined with natural silk, cotton, or schappe. It is used more especially in the woof, and if a drop of water falls upon the thread in the skein it may diminish its tenacity or resistance, but this same water cannot act upon the woven material.

The mixture of a number of textiles, as in Armure, thus makes a sort of a protected material and renders it physically impossible that the water should spread through to injure the material, since only a small part of it is exposed to contact with water, the rain, or the moisture of the atmosphere. Moreover, experience has demonstrated that this is a question of no importance, and it may be said that this is simply a prejudice. However, there is room for improvement here, and our chemists are perseveringly studying this question. They have already achieved some important results, and it is altogether probable that this prejudice concerning the effect of water will be removed in a few months.

This artificial silk is employed usually in the woof in goods manufactured for the Orient, where brilliant coloring is admired; it is also used for lining for scarfs, skirts, mixed cottons, and for upholstery. It has even been employed in taffetas and in umbrella covers, which is a positive answer to the objection that it will not stand water. At present there is a demand in the United States for a sort of heavy tulle made of ovale of 500 deniers of artificial silk coming from France. This material will be fashionable next season, being used on dresses as a trimming over a foundation of satin or taffetas.

The actual daily production of artificial silk amounts to about 44,000 pounds. About 30,000 hands are employed in the works manufacturing this material. It is exported chiefly to the United States and Germany, and it is reported that some is sent to Japan. This refers to the exportation of the thread and not the manufactured article.

I calculate that the total annual American consumption purchased from France, Germany, and Italy is about 882,000 pounds, but it may be half again as large, for this silk is employed in many kinds of textiles

It must be borne in mind that in the present condition of science and industry we cannot expect to have cheaper raw material than this wood paste.

I base my opinion of the future consumption on the fact that to-day the minimum consumption is from 39,700 to 44,100 pounds per day, and this at an average price of \$3.28 to \$4.25 per kilo (2.2 pounds), according to the quality. The result is that when producers are satisfied with a reasonable profit, or when the demand will not be far ahead of the production, the price will fall to \$2.30 or \$2.90. Artificial silk can be used in mixed goods in all the great markets for cotton in general and in all the textile markets. On the other hand, I do not think that, considering the present cost of living, there is any reason to expect a decline in the cost of silk. In short, it must be admitted that some of the adverse criticisms uttered concerning artificial silk are absurd when we remember that it is the same process that the natural silk goes through, as carried on in our laboratories, where natural silk is charged with metal, frequently 80 per cent., and even 200 per cent.

Other silk men of Lyon have expressed the opinion that the high wages ruling in the United States should not be an obstacle to the successful prosecution of the artificial silk industry in that country. This industry is comparatively new and developments may be expected in the work at any moment, as a number of chemists are engaged in trying to perfect the process.—*U. S. Consular Report*, March 17, 1909.

The Bleaching Process.

In compliance with instructions from the Bureau of Manufacturers, Special Agent Davis made inquiries in regard to the process of bleaching flour in Europe, and reports as follows:

I am now in position to state that there is no law in France, Germany, or Great Britain prohibiting or regulating the bleaching of flour by chemical or electrical process. As in the United States, some millers in all the countries named oppose bleaching, or find no need for it, while others employ it.

Recently the Alsop Company (electrical process) was sued by the Andrews Company (chemical process) before the Lille (France) tribunal. The case went to the court of appeals, which has rendered its decision incidentally affirming that the bleaching of flour was an improvement, and that it was not injurious to public health.

Mining and Minerals, Canada.

Consul-General William Harrison Bradley, of Montreal, forwards the following report on mineral production in Canada:

In the following statement are given the quantities and values of mineral products of Canada for 1908, as reported by the Minister of the Department of Mines before a meeting of mining engineers in the city of Montreal:

Metallic Products

Classification.	Quantity.	Value.
Copper, pounds	64,361,636	\$ 8,500,885
Gold	......	9,559,274
Pig iron from Canadian ore, tons	99,420	1,664,302
Lead, pounds	45,725,886	1,920,487
Nickel, pounds	19,143,111	8,231,538
Cobalt, pounds	1,853,286	112,253
Silver, ounces	22,070,212	11,667,197
Total	......	\$41,655,936

(*To be continued*).

CORRECTION.

On page 223, March number, in the abstract "Modern Electric Pyrometry," 8th line, read "The accuracy even at 1200 C. is within 2 to 5 degrees" instead of "2 to 5 per cent." as printed.

For title of third article under *Notes*, April No., p. 260, read "A Simple Rapid Process Vinegar Generator for 'Experimental' Use instead of 'Generator'."

Remove the word "not" from the fifth line from bottom, second column, page 260, April No.

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EDITORIALS.

THE DEVELOPMENT OF INTENSELY WORKING APPARATUS IN CHEMICAL ENGINEERING.

THE beginnings of the study of chemistry were various experiments which consisted in placing different substances together in the same vessel and noticing the effect produced, if any, under varying conditions, of these substances upon each other. The vessels, of course, were of different kinds and the substances were sometimes solids, sometimes liquids and later on, gases or combinations or mixtures of these. The result was in some cases found to be something of sufficient value to warrant the repeating of the experiment upon a larger scale and the development in this way of a process.

The natural form taken in this development was a simple enlargement of the apparatus with the substitution of some other material, if the material of which the original apparatus was made would not lend itself to the construction of a larger apparatus.

Many of the first chemical industrial plants amounted to very little more than a multiplication of the dimensions of laboratory apparatus, and many are still substantially this. As more possibilities began to be discovered in the laboratory, other forms of apparatus were used and here again the industrial apparatus showed a tendency to follow very closely the form of the original laboratory apparatus.

Gradually, in many cases, it began to be seen that, by carefully studying the reactions and physical phenomena accompanying certain processes, it was possible to design very much more efficient apparatus of far greater capacity and produce more certain and better results. This was the beginning of the development of intensely working apparatus. As the apparatus becomes more intensely working, it becomes smaller, the requirements for accuracy in its construction become greater, the use of more appropriate materials in its construction becomes possible, and while sometimes at first the apparatus seems to become more complicated, generally in the end, it is discovered that the apparent complications are in reality simplifications and very great reductions in the cost and size of apparatus per unit of material passed through.

The designer of intensely working chemical apparatus, finds himself in need of knowledge of a branch of chemistry which has not been well explored. He needs to know the conditions governing the rapidity of chemical reactions. For instance, many reactions are considered to require time for their accomplishment, whereas in reality the time is but that required for thorough mixing, and for the molecules to be brought into the necessary proximity to react on one another. When this is the case, the rapidity of many reactions can often be hastened by the application of some form of energy so that the designer of intensely working apparatus must know when this can be done, and to gain this knowledge the only method, as a rule, is to himself investigate the unexplored field, and with the knowledge thus gained to design smaller

and better chemical apparatus, which are likely to be continuous-working and in which reactions which may have previously been considered unavoidably slow, take place instantly.

Is there not here a great field and are not the results to be looked for from efforts in this direction second only to results from the discovery of new substances and new forces?

FRANCIS I. DUPONT.

CALORIMETER STANDARDIZATION.

THE great demand for the calorific value of fuels has, within the past few years, changed its determination from a scientific to a commercial proposition. The result is that for each laboratory that had a calorimeter fifteen years ago there are probably a hundred so equipped to-day. With this extended use there are also greater discrepancies between the results obtained in different laboratories.

A prominent chemist sent portions of the same pulverized sample to ten different laboratories some time ago and received such a variety of results that his confidence in calorimetry was badly shaken.

The buying of coal on a heat unit basis has been greatly handicapped on account of the discrepancies in the results obtained in different laboratories as well as different times in the same laboratory. There is a prevalent idea that the calorific values used for practical purposes need not be as accurate as those used in scientific work, and that any type of calorimeter, kind of thermometer or method of operation will give at least comparable results. This is by no means true, and many plants that have depended upon such results as a guide in selecting the most economical coal would have been better off had they based the comparison on the proximate analysis alone.

Boiler efficiencies are often reported absurdly high or low on account of erroneous calorific determination of the fuel used.

It is in the buying of coal on a heat unit basis that the greatest accuracy is required. A man may use any kind of measuring stick he wishes so long as the results are for his own personal use, but when he buys or sells dry goods, groceries, coal or any other commodity his unit of measurement or weight must conform to fixed standards. In buying coal the weight is not of more importance than is the calorific value. The two are on the same basis and in many contracts one affects the cost of fuel just as much as does the other. If one standard is fixed by law it is certainly unjust to allow the other to be a matter of chance. The heat unit itself is sufficiently well defined, but in a calorimeter determination what assurance has the chemist that the indicated rise in temperature is correct? Very few thermometers graduated to 1/50 or 1/100 degree can be used without corrections being applied. There is necessarily some radiation loss and the methods used in different laboratories for this correction may cause an error of 1 per cent. in the final results. The temperature of the calorimeter itself is raised as well as that of the water, and the accuracy with which its water equivalent has been determined affects every determination. In the operation of the calorimeter great skill and care are required even with a calibrated and standardized instrument. All laboratories have not taken these precautions and their results are discordant, and cause not only a great deal of controversy regarding the true value of coal, but oftentimes unjust penalties and premiums to be exacted.

There are very few contracts on a heat unit basis where 1 per cent. does not mean at least $1,000 per year and in many of them it corresponds to as much as $10,000. Here is where accuracy is of greater importance in practical than in scientific work, at least it is of enough importance to warrant the purchase of a good reliable calorimeter and thermometer and have the water equivalent properly determined and the thermometer carefully calibrated. The United States Bureau of Standards is prepared to do the latter at a nominal charge and they also supply pure cane sugar of known heating value that can be used in determining the water equivalent.

Accuracy is well within the reach of all chemists who care to do high-grade work, and those who continue to report inaccurate results should be considered as much criminals as the man who gives short weight.

E. G. BAILEY.

ORIGINAL PAPERS.

EXPERIMENTS ON THE PUTRESCIBILITY TEST FOR SEWAGE AND SEWAGE EFFLUENTS.

By D. D. JACKSON AND W. A. HORTON.

Received February 10, 1909.

A sewage or sewage effluent is putrescible if, on standing for a certain length of time, it loses

all of its available oxygen. Putrescence takes place when all the dissolved oxygen and the oxygen of the nitrates and nitrites has been used up, and the liquid still contains organic matter available for bacterial action. To determine quantitatively the amount of oxygen required to prevent putrescence, varying amounts of water, the oxygen content of which is known, can be added to the liquid to be tested till that liquid on standing is shown to contain an excess of free oxygen or oxygen in the form of nitrites or nitrates.

Many methods have been proposed and used to determine whether or not a given liquid was putrescible, and considerable variation in the results has been obtained according to the methods employed. A careful study of these methods was therefore undertaken in order to determine their relative sensitiveness, and the method which appeared to give the most concordant results. In this study a large number of sewages and sewage effluents of varying character have been tested by a series of dilutions and with different indicators.

The Odor Method.—In 1895 one of the authors made a long series of putrescibility tests of the sewage and sewage effluent at Worcester, Mass., under the direction of Mr. Harrison P. Eddy, at that time City Superintendent of Sewers. In these tests gallon bottles were used and varying dilutions of river water employed. By the use of these large bottles, the point of putrescibility could readily be determined by the odor. It was found that quicker and better results were obtained when the bottles were kept in a 37° incubator. A large number of bottles could not be used at one time, however, on account of the incubator space required, and the size of the bottles was reduced with a corresponding difficulty in properly determining the odor.

Decolorization Methods.—The methylene blue test as originally devised by Spitta[1] and improved by Spitta and Weldert,[2] removes the necessity for the use of large bottles and gives practically the same results on bottles of 250 cc. capacity, taking the decolorization as an indicator of putrescibility. By the use of this indicator the 37° incubator can be employed to advantage. The space required is small and, as has been also pointed out by Phelps and Winslow[3] and by Johnson, Copeland and Kimberly,[4] the time necessary for the test is only one-half that which would be taken if the bottles were kept at room temperature.

The only criticism of the use of the 37° incubator is in the leakage which sometimes occurs around the stoppers of the bottles, due to the expansion of the liquid when the temperature is raised, which loosens the stopper and may drive out some of the originally dissolved gas. This is occasionally followed by a backward leakage of air. The authors have experimented with various devices for preventing this leakage and have found a simple and most effective arrangement. The test is made by replacing the ground glass stopper of a 250 cc. bottle by a perforated soft rubber stopper through which is a small glass tube or medicine dropper having a heavy rubber cap of about 5 cc. capacity tightly attached to the end. The tube is drawn out like the usual medicine dropper and when in position extends into the liquid in the bottle. A measured amount of the colored indicator is placed in the bottle, which is then completely filled with the liquid to be tested. The dropper is then also completely filled with the liquid, making sure that no air bubbles are left. The tube which

DEVICE FOR PUTRESCIBILITY TESTS.

extends through the stopper is placed in position and the excess of water pressed out between the bulb and the top of the tube, leaving the bulb in a collapsed state.

When placed in the incubator the bulb will partially fill, due to expansion of the liquid and the giving off of some gas previously in solution. By this method the expanded water and all gas bubbles are held back and there is no loss of the original water or air in solution.

The accompanying illustration shows the rubber stoppered bottle with the tube and bulb in position. The best and most durable tube and bulb for this purpose is made by the Tyer Rubber Company, 27 Duane Street, or may be obtained from Eimer & Amend, New York City.

A Comparison of Indicators.—In a recent article, Clark and Adams[5] have compared methylene blue, methylene green, indigo carmine, and fourteen other dyes of less importance and have decided that the methylene green and indigo carmine are the most satisfactory indicators for use at a temperature of 27° C. Inasmuch as their experiments were made at that temperature instead of at blood heat, the authors decided to repeat this work, using the 37° incubator.

While dilutions may be made with tap water or river water, the best comparative results are obtained when using distilled water at 20° C. saturated with air. Such a water contains 9.2 parts per million of oxygen and should be used in standard work where close comparative results are required. The varying amounts of organic matter, nitrites, and especially nitrates in natural waters used for dilution work, may materially affect the highest point of dilution at which putrescence will occur.

The following table gives some of the relative results obtained using the double zinc salts of methylene blue and methylene green in amounts of one cubic centimeter to a 0.05 per cent. solution to the 250 cc. bottle of the sample and an equal color depth (one cc. of the same dilution) of indigo carmine.

The samples were kept in all cases for longer periods of time than given in the table but no change occurred beyond the days noted.

The results of our experiments show that at the temperature employed the indigo carmine did not always give satisfactory figures and was delayed in its action, while the methylene blue was not quite as delicate as the methylene green. There is, therefore, some reason for changing the indicator generally employed, and we would recommend the use of the methylene green as being of slightly greater delicacy.

	Days.	Methylene blue, highest dilution, putrescible.	Methylene green, highest dilution, putrescible.	Indigo carmine, highest dilution, putrescible.
Brooklyn sewage, Fulton Street	1	1–8	1–12	1–6
	2	1–13	1–13	1–11
	3	1–15	1–15	1–14
	4	1–16	1–18	1–16
	5	1–17	1–18	1–16
Bedford sewage, N. Y. Reformatory septic effluent.	1	1–5	1–5	1–2
	2	1–6	1–6	1–5
	3	1–7	1–7	1–5
	4	1–7	1–8	1–5
	5	1–8	1–8	1–5
Gowanus Canal, Brooklyn.	1	1–2	1–3	1–2
	2	1–3	1–4	1–3
	3	1–3	1–4	1–3
	4	1–4	1–5	1–4
	5	1–4	1–5	1–4
Uncontaminated mud from bottom of Massapequa Pond.	1	Undiluted	Undiluted	Undiluted
	2	1–1	1–1	Undiluted
	3	1–2	1–1	Undiluted
	4	1–4	1–4	1–1
	5	1–4	1–4	1–1
	6	1–4	1–4	1–1
Uncontaminated mud from bottom of East Meadow Pond.	1	Undiluted	Undiluted	0
	2	1–1	1–1	0
	3	1–1	1–1	Undiluted
	4	1–1	1–1	Undiluted
Jamaica, L. I. City sewage.	1	1–4	1–5	1–5
	2	1–5	1–6	1–6
	3	1–7	1–8	1–7
	4	1–7	1–8	1–7
Jamaica, L. I. Effluent from lime treatment.	1	1–1	1–2	1–1
	2	1–2	1–2	1–2
	3	1–2	1–3	1–2
	4	1–2	1–2	1–2
Bedford, N. Y. Septic tank effluent.	1	1–11	1–12	1–6
	2	1–11	1–12	1–10
	3	1–11	1–12	1–10
	4	1–11	1–12	1–10
Bedford, N. Y. Sprinkling filter effluent.	1	Undiluted	1–1	Undiluted
	2	Undiluted	1–1	Undiluted
	3	Undiluted	1–1	Undiluted
	4	Undiluted	1–1	Undiluted

Contrary to the usual belief, we found that variations in the amount of coloring matter used made noticeable differences in the point of putrescibility. The following table gives the results obtained on varying quantities of the three indicators when 0.1 per cent. solutions were employed.

It will be seen from the figures below that all three of the indicators used are slightly antiseptic so that it is best to employ the indicator in amounts as small as is possible to obtain a distinct color. These amounts are, in the case of methylene blue and methylene green, one cubic centimeter of a one-twentieth of one per cent. solution for each bottle of 250 cc. capacity, and for indigo carmine, one cubic centimeter of a one-tenth of one per cent. solution.

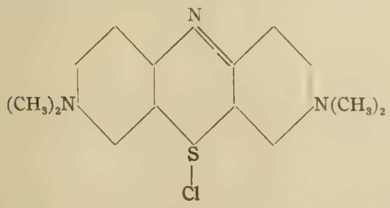
	Days.	Methylene blue, highest dilution, putrescible. 1 cc.	1/2 cc
Brooklyn sewage, South Ferry	1	1–11	1–12
	2	1–14	1–16
	3	1–16	1–18
	4	1–20	1–20

	Days.	Methylene green, highest dilution, putrescible. 1 cc.	1/2 cc.
Brooklyn sewage, South Ferry	1	1–13	1–14
	2	1–14	1–18
	3	1–16	1–18
	4	1–20	1–20

	Days.	Indigo carmine, highest dilution, putrescible. 2 cc.	1 cc.
Brooklyn sewage, South Ferry	1	1–6	1–8
	2	1–12	1–14
	3	1–16	1–17
	4	1–18	1–20

It was thought possible that medicinal methylene blue, which is the chloride free from zinc, might be a better indicator than the common methylene blue, which is the double zinc salt. This latter salt is the coloring matter which has been generally used for the putrescibility test.

In composition the medicinal salt is the chloride of tetramethylthionine ($C_{16}H_{18}N_3SCl$) with the formula:



At the same time these salts were also compared with methylene green. This latter substance is always bought as the double zinc salt, as there is at present no commercial use for the chloride. It is double zinc salt of mononitromethylene blue.

The following are the results obtained by a comparison of these three indicators using in each case one cc. of a 0.05 per cent. solution to the 250 cc. bottle.

It will be seen from these results that the medicinal methylene blue is not as delicate an indicator as the double zinc salt or commercial variety and that the methylene green is slightly more delicate than the commercial methylene blue.

These differences are probably due to molecular construction. The zinc salts would tend to be more easily broken down under anaerobic conditions and the methylene green would have a greater tendency to be acted upon as it is a mononitro derivative of methylene blue and for this reason may be considered to have a slightly weaker point of attack.

	Days.	Methylene blue. Medicinal chloride.	Methylene blue. Commercial double zinc salt.	Methylene green. Commercial double zinc salt.
Montefiore, home sewage, from septic tank, Bedford, N. Y.	1	1–12	1–13	1–13
	2	1–12	1–13	1–14
	3	1–13	1–14	1–14
	4	1–14	1–14	1–14
Montefiore, home sewage from effluent of sprinkling filter.	1	Undiluted	1–1	1–1
	2	1–1	1–2	1–2
	3	1–2	1–2	1–2
	4	1–2	1–2	1–4
Jamaica, L. I., city sewage.	1	1–5	1–5	1–6
	2	1–6	1–7	1–8
	3	1–8	1–9	1–9
	4	1–9	1–9	1–9
Jamaica, L. I., effluent from lime treatment.	1	Undiluted	1–1	1–2
	2	1–1	1–1	1–2
	3	1–2	1–2	1–4
	4	1–3	1–3	1–4

In treating undiluted sewages with these three indicators the methylene green was always decolorized first, then the zinc salt of methylene blue, and finally the medicinal methylene blue. This shows clearly the degrees of delicacy of the three indicators.

The indigo carmine was usually last to be acted upon, but this was not always the case. There seems to be much variation in the action of this indicator, depending upon the nature of the sewage or effluent employed. There is also great variation in the salt itself as found on the market, as it is composed of the more or less pure sodium salt of indigotine disulphonic acid or the free acid itself.

In waters containing much suspended inorganic matter, it sometimes happens that the coloring matter is precipitated or dragged down to the bottom of the bottle and the liquid above becomes colorless. Such a result should not be mistaken for putrescence, as when the bottle is shaken the indicator will become suspended and will be shown not to have been decolorized.

Some authors have criticized the indicator test as giving positive results at times when no disagreeable odor is developed. It is probable that in such cases the air is entirely used up in the bottle, but the excess of organic matter is not sufficient to develop a much further increase in bacterial ac-

tion, so that while anaerobic conditions exist, the odor does not sharply indicate the fact. In at least one case the odor of such a sample could be obtained by incubating a gallon bottle and then pouring out a portion of the liquid and shaking the bottle. In this case a strong odor became evident, which would otherwise have been undetected.

Putrescibility and Bacterial Action.—In this connection a series of experiments on the amount of bacterial action produced in waters and sewages of various organic contents is of interest. The following samples kept at 20° C. were examined daily for bacteria:

No. 1. Highland Spring Brewery, Boston, Mass. Well 750 feet deep.

No. 2. Highland Spring Brewery, Boston, Mass. Well 50 feet deep.

No. 3. Norfolk Brewery, Boston, Mass. Deep well.

No. 4. Burton Brewery, Boston, Mass. Deep well.

No. 5. Worcester sewage, branch sewer after heavy rain. Diluted with distilled water, one part of sewage to 100 parts of distilled water.

No. 6. Same as No. 5, only not diluted.

No. 7. Strong sewage, branch sewer, Worcester, Mass.

No. 8. Undiluted urine seeded with bacteria.

The results are given in the order of the increasing albuminoid ammonia present and the bacterial action, while not in proportion to the albuminoid ammonia, is shown to follow it in a general way, indicating that such action is in proportion to the available organic matter. If this action is sufficient to use up the oxygen in the water and reduce the nitrates and nitrites, then the water is putrescible.

The table below shows that only in the last three samples the organic matter available as food for bacteria was sufficient to produce anaerobic conditions and putrescence at the points marked by stars, while in the first five samples the organic matter present was insufficient to produce such a result.

Experiments on pure cultures showed that B. cloaceae and B. proteus Zenkeri produced stronger odors than did B. coli and that the odor developed varied in strength, not only with the amount but with the nature of the organic matter present.

	No. 1. Albuminoid ammonia. Parts per mil. 0.002. Bacteria per cc.	No. 2. Albuminoid ammonia. Parts per mil. 0.007. Bacteria per cc.	No. 3. Albuminoid ammonia. Parts per mil. 0.009. Bacteria per cc.
Start	10	6	24
1 day	11	18	350
2 days	11	132	1,140
3 days	11	138	1,395
4 days	10	284	1,025
7 days	3	176	580

	No. 4. Albuminoid ammonia. Parts per mil. 0.014. Bacteria per cc.	No. 5. Albuminoid ammonia. Parts per mil. 0.032. Bacteria per cc.	No. 6. Albuminoid ammonia. Parts per mil. 3.200. Bacteria per cc.
Start	4	810	81,000
1 day	1,450	5,000	9,280,000
2 days	2,700	16,000	18,020,000
3 days	10,500	493,000	85,500,000*
4 days	3,630	5,480,000	22,100,000
7 days	2,820	3,613,000	1,900,000

	No. 7. Albuminoid ammonia. Parts per mil. 44.800. Bacteria per cc.	No. 8. Albuminoid ammonia. Parts per mil. 210.000. Bacteria per cc.
Start	250,900	35,600
1 day	72,540,000*	2,270,000
2 days	475,000,000	11,540,000
3 days	5,580,000,000	43,000,000*
4 days	19,530,000,000	3,780,000,000
7 days	4,278,000,000	25,110,000,000

CONCLUSIONS.

1. The test for putrescibility, if made by taking the odor, requires bottles of large size and an incubator space too great to be practical. As the bottles must be completely filled with the varying dilutions of the sewage or effluent and cannot be shaken except at the end of the test, a comparison of the time required to become putrescible cannot be readily made. The delicacy of the test in general is not as great as by the use of color indicators.

When the standard comparative results are required the dilutions should be made with distilled water at 20° C. saturated with air.

2. The test is best made in bottles of 250 cc. capacity, having perforated rubber stoppers, in which are inserted medicine droppers with tight rubber bulbs. This bulb compensates for any change in volume due to the expansion of the liquid and prevents loss of water or previously dissolved gas.

3. The test should be made in an incubator at 37° C., using the double zinc salt of methylene green as an indicator and the standard results

* NOTE.—Odor developed and putrescence began.

taken at the end of four days. In the regulation of sewage filters practical comparative results may be obtained in a much shorter period. In sewage laboratories where only rough tests are required, the room temperature may be used, in which case eight days may be taken as the standard time of incubation but, as in the case of the 37° tests, practical results may be had in much shorter periods of time.

The amount of methylene green used should be one cc. of a solution containing one-half a gram per liter. Larger amounts of this, as well as of methylene blue, have a slight antiseptic action.

4. The comparison of the relative putrescibility by dilutions of sewages and effluents is a very valuable test of the various methods of sewage treatment. It not only tests the work accomplished by purification plants but gives data as to the amount of dilution necessary to prevent foul odors in the final disposal of a sewage or effluent which enters a stream or other body of water.

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MOUNT PROSPECT LABORATORY,
BROOKLYN, N. Y.

CONTRIBUTION ON THE CHEMISTRY AND PHYSICS OF JELLY-MAKING.

By N. E. GOLDTHWAITE.

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The object of these experiments has been to determine as exactly as possible the conditions necessary for the formation of fruit jellies. These conditions are doubtless well known to the manufacturers of fruit products, but diligent search of chemical literature has failed to disclose articles dealing directly with the subject in hand.

Bigelow's admirable review[1] of the work done on the chemistry of pectin bodies, emphasizes the fact that as yet little has been definitely ascertained concerning the constitution and function of these compounds. The experimental results indicate in general that these pectin bodies are carbohydrates. Herzfeld[1] regarded them as combinations of araban and galactan, and Tollens[2] has suggested that they may be glucosides.

Though the constitution of these bodies is so far from being determined, yet their fundamental physical characteristic—that of forming jellies under certain conditions—has long been well known practically. Our quest in the present work is to find the conditions under which this gelatinizing power best manifests itself, *i. e.*, the conditions under which pure fruit jellies of the best texture are formed. Bigelow's arbitrary method for making jellies[3] by boiling together equal parts of fruit-juice (more or less diluted with water) and of cane-sugar, for 20 minutes, does not, in our experience, necessarily yield jellies of a uniformly good texture. By a jelly of good texture we mean one obtained by so treating fruit juice that the resulting mass will quiver, not flow when shaken—one which can be cut easily with a spatula, the angles so produced preserving thejr shape when a piece is isolated, and yet one which is not tough.

I. Method of Procedure.—Since the present work was begun in September, 1908, the jellies so far investigated have been made from fall fruits only. In extracting the juices for these jellies any unsound portion of the fruit was removed and the sound portion cut into small pieces if possible. The fruit so prepared was barely covered with cold distilled water (about 1 liter, or less, to 2 kgs. of prepared fruit) and the whole brought slowly to the boiling point and kept simmering until the fruit was thoroughly cooked. The mass was then removed to a filter made of a double fold of cheesecloth and allowed to drain completely. It was found that the pulp remaining on the filter could be again boiled up with water (the least amount possible) and that the resulting juice would make a good jelly. This was particularly true in the case of grapes, even the fourth and fifth extractions making an excellent quality of jelly—a quality better than that made from the first extraction because potassium acid tartrate crystals did not appear in it as is usual in the case of jelly from grapes.

[1] *Bureau of Chem., Bull.* **94,** 67–87.

[1] *Zts. Ver. d. Zuckr. Ind.* **41,** 295, 667 (1891).

[2] *Ann.*, **286,** 292 (1895).

[3] *Jour. Am. Chem. Soc.*, **23,** 347. *Bureau of Chem., Bull.* **66,** 50.

Naturally, considering the nature of our problem, we followed no set method for making our jellies, but varied our methods within wide limits, *e. g.*, we varied the acidity of the fruit juice from a neutral condition to 0.669 per cent. of acid; the amount of sugar used from none to 2 volumes per 1 volume of juice; the time of boiling sugar with juice from the whole time of cooking to the last five minutes only. The total time of cooking was always limited to the time when we obtained a good jelly test, *i. e.*, when a portion of the hot liquid would jell as it was dropped from a cold metal spatula.

II. Necessary Constituents of Jelly. (*a*) *Pectin.*—Braconnot, who first investigated pectin, pointed out[1] that very palatable jellies could be produced from the alkaline pectates which he isolated from carrots by treating the latter with alkalies. He made jellies by dissolving these alkaline pectates in water, heating with sugar and then adding a small quantity of a mineral acid.

Although the jelly-maker never handles directly such alkaline pectates or even pectin itself, yet it has long been recognized that the first essential constituent of a fruit juice for making jelly is this latter body—pectin. Its presence in a given juice is readily ascertained by adding to a portion of the juice an equal volume of alcohol, shaking and cooling; a gelatinous precipitate filling a considerable portion of the total volume of the liquid indicates pectin. Good jelly-making consists in so controlling conditions as to cause this pectin to be precipitated evenly throughout the total volume of liquid allowed it. That it can be precipitated by alcohol, various metallic salts, acids and sugar was discovered by Braconnot.

(*b*) *Acid.*—The second essential constituent of fruit juice for making jelly is acid. This fact may be proved in a twofold manner. First, negatively, *e. g.*, when the acid of a primarily good jelly-producing juice is neutralized, no jelly can be made from the resulting juice although it contains plenty of pectin; second, positively—if a juice which contains pectin, but which in its natural condition will yield no jelly, be acidified properly, a good jelly may be produced.

Negatively, the necessity of acid in a jelly-making juice was proved as follows: A given quantity of crab-apple juice was divided into three equal portions. Of the first portion an excellent grade of jelly was produced, using an equal volume of sugar, boiling the juice 10 minutes before the addition of the sugar and 20 minutes thereafter, *i. e.*, till the jelly-test was obtained. To the second portion of juice a sufficient quantity of N/10 NaOH was added to just neutralize the acid present, and then an attempt made to make jelly as above. Result, a dark colored thick, fruit syrup which never gave any signs of forming a jelly, but from which cane-sugar crystals were slowly deposited. To the third portion of juice sufficient N/10 NaOH was added to neutralize half the acid present, the subsequent treatment corresponding to the above. Result, a thick fruit syrup which never showed any signs of jelly formation although at the end of four months pectin could be precipitated abundantly by the addition of alcohol.

[1] *Ann. de Chim. et. de phys.* [2]. **28**, 173 (1825); *Ibid* [2]. **30**, 96.

Experiments corresponding to the first and second of these cases were carried out with grape juice, with exactly analogous results. That the juices contained plenty of pectin is evident from the fact that in their natural state they easily yielded jellies.

These experimental results are summed up in Table I:

TABLE I.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	Per cent. of acid in juice (calc. as H_2SO_4).	Proportion of cane sugar to juice by vol.	Time of boiling. Before adding sugar. Min.	Time of boiling. After adding sugar. Min.	Texture of jelly.
5	Crab-apple	1.043	0.550	1 : 1	10	10	Excellent
6	Crab-apple	1.043	0.000	1 : 1	10	10	Syrup
7	Crab-apple	1.043	0.275	1 : 1	10	10	Syrup
126	Grape	1.025	0.313	1 : 1	30	10	Excellent
127	Grape	1.025	0.000	1 : 1	30	10	Syrup

Nos. 5 and 126 represent respectively crab-apple and grape juices in their natural condition from which excellent jellies were easily prepared. Nos. 6 and 127 represent these same juices after neutralization from neither of which could jelly be made. Though No. 7 represents only a half-neutralization of crab-apple juice yet this also refused to yield jelly. It should be noted that the low sp. gr. and acidity of the grape juice used in these experiments is due to the fact that this juice was composed of the later extractions of the pulp. On account of this low sp. gr. a considerably longer time for boiling was necessary, but for reasons shown further on, this preceded the addition of the sugar.

Positive proof concerning the necessity of acid for the formation of jelly may be cited as follows: Sweet apple, pear and peach juices contain an abundance of pectin as is evident from the alcohol test, yet under ordinary conditions it was found impossible to produce jellies from these juices.

However, addition of an organic acid to each juice so modified conditions that a very fair jelly could be made as shown in Table II:

TABLE II.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	Natural % of acid in juice (calc. as H_2SO_4).	Acidity of juice after addition of acid.	Proportion of cane-sugar to juice by volume.	Time of boiling: Before adding sugar. Min.	Time of boiling: After adding sugar. Min.	Texture of jelly.
80	Sweet apple	1.042	0.098	0.098	¾ : 1	10	20	Syrup
110	"	1.042	0.098	0.308	"	20	7	Fair jelly
111	"	1.042	0.098	0.395	"	20	7	Good jelly
112	"	1.042	0.098	0.552	"	20	7	Very good
117	"	1.037	0.098	0.675	"	20	10	Fair jelly
106	Pear	1.047	0.284	0.284	"	20	10	Syrup
100	"	1.047	0.284	0.405	"	20	10	Syrup
105	"	1.047	0.284	0.511	"	20	10	Good jelly
150	Peach	1.033	0.311	0.311	"	20	10	Syrup
151	"	1.033	0.311	0.575	"	20	7	Fair jelly

Examination of this table shows that the texture of these jellies was best when the acidity corresponded to about 0.5 per cent. for juices whose sp. gr. was about 1.04. It is interesting that this acidity and sp. gr. correspond in general to those of crab-apple juice, the best natural juice for jellies so far investigated in these experiments. Increasing the acidity of these juices beyond about 0.5 per cent. seemed to impair the texture of the resulting jelly, as is evident from No. 117.

III. Discussion.—It appears then that through this addition of an organic acid to a fruit juice containing naturally little acid, jellies can be made if these juices contain pectin. However, the flavor of the fruit is generally changed; the sweet apple jelly so made tasted much like that made from sour apples, the tartness of course increasing with increasing percentages of acid; the flavor of the pears, in pear jelly, was fairly well preserved, while in peach jelly the peach flavor was completely destroyed. Repeated experiments, varying the percentages of acid were made in an endeavor to preserve the peach flavor, but success was not attained in this respect, though a jelly of fair texture could be produced. From experiments testing the relative merits of tartaric and citric acids in connection with the use of one or the other to acidify a fruit juice, the balance of favor seemed to be with the former. Both texture and flavor of jellies made by its use were superior to those in which citric acid was used. Nos. 151 and 152 in Table V represent tests in which tartaric acid was the acid added, while in Nos. 153 and 154 citric acid was used. The method of making Nos. 151 and 153 corresponds, likewise Nos. 152 and 154. There was no question concerning the superiority of Nos. 151 and 152, *i. e.*, the jellies made by the help of tartaric acid.

That a mineral acid like hydrochloric can be substituted for an organic acid was demonstrated. While this is interesting from a chemical standpoint, it naturally would not be recommended in the preparation of fruit jellies for food.

In determining the acidity of fruit juice better end-reactions were obtained when the juice was titrated *into* the $N/10$ alkali (using phenolphthalein as an indicator) rather than the reverse as is usual. In the case of grape or plum juices no indicator was necessary, but the titration was best carried out titrating the N/10 alkali into a definite volume of the juice (well diluted) and taking as the end-reaction that point at which the pink color of the liquid just merged into green.

That no acid disappears as such in the preparation of jellies was proved by the following experiments: Crab-apple juice (100 cc. acidity = 0.532 per cent.) was made into jelly using an equal vol. of sugar. The resulting unskimmed jelly was dissolved in distilled water, diluted to 500 cc. and the acidity again determined. The acidity of this dissolved jelly was found to be 0.107 per cent., or, if calculated in terms of the original volume of juice (100 cc.) it equaled 0.535 per cent. This is identical with the original acidity (0.532 per cent.) within the limits of experimental error.

Experiments substituting lime-water and also calcium salts as a precipitant of pectin in making jellies from sweet fruit juices were carried out. However, good jellies have not so far been obtained by this method.

It was found that glycerin could be used in place of sugar in the making of crab-apple jellies. The jellies so made were of excellent texture and of fair taste and they had remarkable keeping qualities.

When glycerin and sugar were used simultaneously with peach juice, a fair jelly was produced, but from this sugar subsequently crystallized out. These crystals were remarkably large and perfect.

IV. Sugar in Jelly-making.—That so-called jellies can be produced by merely boiling down fruit-juices is well known. Naturally the flavor of such a jelly is decidedly fruity, but in texture it is very tough. The making of such jellies requires a large amount of juice, *e. g.*, we found to make one glass of such apple jelly required a volume

of juice sufficient for six glasses when made with sugar. Ordinarily, sugar is cheaper than fruit juice, so from the standpoint both of palatability and of economy (possibly also of digestibility) jellies made with sugar are preferable.

(*a*) *Amount of Sugar.*—The proportion of sugar to juice is a somewhat difficult one to decide. Experimental results indicate that it depends more upon the proportion of pectin present in a juice than upon any other one factor. It seems probable that in the actual practice of making jellies poor results are very likely to occur through the use of too much sugar, and this because of the relatively large quantities of water that have been used in extracting the fruit juices. Through using these relatively large quantities of water the jelly-maker is deceived regarding the actual volume of fruit juice, hence the use of an over-abundance of sugar. Fruit juices which have required little water for their extraction, apparently will utilize a larger proportional amount of sugar than those that necessarily have been much diluted with water. Some of these statements will be made clearer from the following records of experiments:

TABLE III

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4).	Volume of juice cc.	Proportion of cane sugar to juice by volume.	Time of boiling. Before adding sugar. Min.	Time of boiling. After adding sugar. Min.	Amount of jelly formed. Grams.	Texture of jelly.
1	Crab-apple[1]	1.0375	0.350	300	¼ : 1	5	15	237	Tough
2	"	1.0375	0.350	300	½ : 1	5	12	316	Good
3	"	1.0375	0.350	300	¾ : 1	5	10	474	Excellent
4	"	1.0375	0.350	300	1 : 1	5	9	553	Too soft
120	Grape	1.066	0.487	300	½ : 1	0	30	266	Tough
121	"	1.066	0.487	300	⅝ : 1	0	30	281	Fair
122	"	1.066	0.487	300	¾ : 1	0	23	382	Good
123	"	1.066	0.487	300	1 : 1	0	20	473	Very good

Note in each of these two series of experiments that with an increasing proportional amount of sugar, the volume of jelly produced constantly increases. Note also that the texture of the grape jelly improves with increasing volume of sugar, while in the case of the crab-apple the best jelly is that in which proportion of sugar to juice is as 3/4 : 1; increasing this proportion of sugar impairs the texture of the jelly. An explanation of these facts concerning the texture of the jelly is suggested when we consider that we are here dealing with a grape juice of high sp. gr. and of comparatively high acidity, but with a crab-apple juice of low sp. gr. and of low acidity, hence this grape juice is able to utilize a larger proportional amount of sugar than the crab-apple juice can.

[1] Both the low sp. gr. and acidity of this crab-apple juice are explained by the fact that it was the fourth extraction of juice.

It may also be noted here that as the proportion of sugar in grape juice increases (and consequently the volume of jelly as shown) the crystals of acid potassium tartrate naturally deposited from this jelly decreased. Possibly the increased volume of jelly from a given amount of juice accounts for this, inasmuch as this increased volume of jelly means a less concentration of the potassium acid tartrate contained in it. This behavior of grape jelly is interesting especially when taken in connection with what has been previously remarked concerning making it from other than the first juice extraction. That too great a proportion of sugar to juice (depending on the sp. gr. and acidity of the latter) impairs the texture of the jelly, is emphasized in Table IV.

TABLE IV.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4).	Proportion of cane sugar to juice by vol.	Time of boiling. Before adding sugar. Min.	Time of boiling. After adding sugar. Min.	Texture of jelly.
115	Sweet apple	1.037	0.675	¾ : 1	20	15	Very good
170	"	1.037	0.675	1 : 1	20	10	Good
171	"	1.037	0.675	1½ : 1	0	15	Poor
172	(½ of 171)	...	....	....	..	15	Poor
173	(½ of 171) + equal vol. of juice			....	..	20	Very good
174	Sweet apple	1.037	0.675	2 : 1	0	15	Very poor

The texture of No. 115 was very good, but increasing the proportion of sugar beyond the proportions used in this experiment resulted in a deterioration of the texture of the jelly. Nos. 171–172 and 174 are striking examples of the use of too great a proportion of sugar. Nos. 171 and 174 were a very poor quality of jelly; pectin was precipitated in lumps throughout the mass, not in a continuous, semi-firm substance as in a good jelly. Subsequent boiling of 171 (*i. e.*, 172) served only to darken the product, but not to improve its texture. However, upon the addition to 171 of an equal vol. of juice (No. 173) and upon further boiling, a jelly fully equal in texture and taste to No. 115 was produced. Evidently then, in making fruit jellies, close attention must be given to the proportion of sugar used. Too little renders the jelly tough, too much (*i. e.*, more than the proportion of pectin present in the juice will warrant) greatly impairs the texture and flavor of the jelly. This latter fact may account more than any other for jelly failures.

TABLE V.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	Natural per cent. of acid in juice (calculated as H_2SO_4).	Per cent. of acid in juice as used.	Weight of juice. Grams	Proportion of cane sugar to juice by volume.	Weight of cane-sugar. Grams.	Time of boiling: Before adding sugar Min.	Time of boiling: After adding sugar Min.	Temperature at which jelly test was apparently observed.	Sp. gr. of hot jelly.	Wt. of jelly + skimmings	Texture of jelly.	Per cent. of cane-sugar found in fruit juice = d.	Per cent. of cane sugar put into jelly = e.	∴ Total per cent. of cane-sugar in jelly = $d + e$.	Saccharimeter readings: Before inversion.	Saccharimeter readings: After inversion.	Temp. at which saccharimeter readings were taken	Per cent. of cane sugar found in jelly = s.	∴ Per cent. of cane-sugar uninverted = $s/(d+e)$.	∴ Per cent. of cane-sugar inverted = $100 - s/(d+e)$.	Crystallization of cane sugar at surface of jelly.
100	Pear	1.047	0.295	0.405	317	3/4:1	190.5	20	10	103.0°	1.28	340.0	Syrup	Undetermined.	56.00	56.00	19.11	-13.39	20.0°	48.50	86.60	13.40	Slight
101	"	1.047	0.295	0.522	316	3/4:1	190.5	20	10	103.0°	1.28	338.4	Thin jelly		56.59	56.59	20.00	-13.03	21.0°	49.48	87.43	12.60	None
102	"	1.047	0.295	0.669	316	3/4:1	190.5	20	10	103.0°	1.28	344.2	Poor jelly		55.34	55.34	15.50	—12.78	20.0°	42.20	76.25	23.75	"
103	"	1.047	0.295	0.669	261	1:1	253.0	20	4	103.0°	1.30	419.5	Fair jelly		60.30	60.30	23.61	—13.47	21.0°	55.55	92.12	7.88	Much
104	"	1.047	0.295	0.669	263	1:1	253.0	0	20	103.0°	1.285	419.5	" "		60.30	60.30	6.04	-12.38	22.0°	27.70	45.93	54.07	None
110	Sweet apple	1.042	0.100	0.308	312	3/4:1	190.5	20	7	103.0°	1.27	346.4	Fair jelly	7.71	55.00	62.71	24.30	-11.20	22.0°	53.30	85.00	15.00	"
111	"	1.042	0.100	0.395	314	3/4:1	190.5	20	7	103.0°	1.27	345.9	Good	7.71	55.00	62.71	21.60	-11.20	22.0°	49.30	78.45	21.55	"
112	"	1.042	0.100	0.552	315	3/4:1	190.5	20	7	102.5°	1.25	356.0	Very good	7.71	53.50	61.21	20.40	-11.16	22.0°	47.40	77.43	22.57	"
113	"	1.042	0.100	0.552	314	3/4:1	190.5	0	26	103.0°	1.26	342.0	Good	7.71	55.70	63.41	2.40	-11.00	23.0°	20.20	31.85	68.15	"
114	"	1.042	0.100	0.552	256	3/4:1	150.0	10	13	103.0°	1.27	263.0	Very good	7.71	57.00	64.71	14.00	-10.94	24.0°	37.80	58.41	41.59	"
120	Grape	1.066	0.487	0.487	316	1/2:1	95.0	0	30	104.0°	1.26	266.5	Tough	Undetermined.	35.00	35.00	—0.30	-10.37	24.0°	15.25	43.57	56.43	Slight(?)
121	"	1.066	0.487	0.487	318	5/8:1	127.0	0	30	103.0°	1.26	281.0	Fair		45.00	45.00	+2.46	—11.15	24.0°	21.30	47.33	52.67	None
122	"	1.066	0.487	0.487	320	3/4:1	190.5	0	23	103.0°	1.26	382.0	Good		49.00	49.00	5.90	—10.64	24.0°	25.06	51.14	48.86	"
123	"	1.066	0.487	0.487	319	1:1	253.0	0	20	103.0°	1.26	473.0	Very good		53.00	53.00	9.64	—11.22	23.0°	31.56	59.54	40.46	"
124	"	1.066	0.487	0.487	298	1:1	239.0	15	4	104.0°	1.30	434.0	Very good		55.00	55.00	18.38	—12.48	23.0°	46.48	84.70	15.30	Slight.
130	Plum	1.033	0.623	0.623	254	1:1	215.0	0	27	103.0°	1.26	365.0	Good	0.0	59.00	59.00	12.60	—9.25	23.0°	33.00	56.00	44.00	None
131	"	1.033	0.623	0.623	254	1:1	215.0	10	10	103.0°	1.26	370.0	"	0.0	58.10	58.10	23.35	-9.90	23.0°	50.18	85.05	14.95	Slight
140	Medium sour apple	1.041	0.257	0.257	259	1:1	210.0	0	22	103.0°	1.27	362.0	Good	0.66	58.00	58.66	20.90	-12.10	21.0°	49.40	84.21	15.80	"
141	" " "	1.041	0.257	0.257	259	1:1	210.0	0	18*	103.0°	1.27	344.0	Good	0.66	61.00	61.66	20.00	—11.77	21.0°	47.50	77.03	23.00	None
142	" " "	1.041	0.257	0.428	259	1:1	210.0	12	13	103.0°	1.28	344.0	Very good	0.66	61.00	61.66	20.00	—12.6	21.0°	48.80	79.11	20.88	Slight
150	Peach	1.033	0.311	0.311	259	3/4:1	159.0	20	10	103.0°	1.29	253.8	Syrup	2.8	62.41	65.21	31.82	—12.18	19.0°	65.18	100.00	0.00	Some
151	"	1.033	0.311	0.575	259	3/4:1	159.0	20	7	103.0°	1.29	263.7	Fair	2.8	60.30	61.11	26.05	—11.05	18.0°	55.63	91.03	9.00	"
152	"	1.033	0.311	0.575	259	3/4:1	159.0	0	29	103.0°	1.28	273.1	"	2.8	57.22	60.02	12.35	—11.18	19.5°	35.05	58.41	41.59	None
153	"	1.033	0.311	0.600	259	3/4:1	159.0	20	7	103.0°	1.28	267.7	Thin jelly	2.8	59.40	60.20	27.30	—11.71	17.5°	56.20	93.35	6.65	Some
154	"	1.033	0.311	0.600	259	3/4:1	159.0	0	32	103.0°	1.28	266.4	" "	2.8	60.00	62.80	16.80	—11.60	18.0°	42.07	67.00	43.00	None

* Hard boiling.

(*b*) *Inversion of Sugar.*—It has been pointed out by Bigelow[1] that the amount of inversion of sugar in jellies and jams varies in general with the length of time of heating, the content of acid, and also the nature of the acid. Experimental data further substantiating these statements are tabulated in Table V.

A word of explanation concerning the data in this table should be given here.

The specific gravity of the juice in each instance was determined by means of a hydrometer. The acidity of the juice either before or after adding more acid was determined as already indicated.

The percentage of cane-sugar put into the jelly was calculated from the weight of sugar added and the total weight of jelly and skimmings obtained. Unfortunately it was necessary to weigh the jelly itself hot.

The percentage of cane-sugar found in the jelly was calculated from the direct and invert readings according to Clerget's formula $S = 100(a-b)/(144 - t/2)$. Polarizations were made upon normal weights of the juices and half-normal weights of the jellies, all the results being calculated to normal weights. Solutions were clarified and inverted according to the method elaborated by Sherman.[2]

Examination of this table shows, as we should expect, that the percentage of inversion of sugar is vastly influenced by the time the sugar and juice are boiled together, *e. g.*, compare No. 103 with 104; Nos. 112–114 with each other; No. 123 with 124; No. 130 with No. 131; No. 151 with No. 152; and No. 153 with No. 154. Note in these comparable cases that the proportional amounts of sugar and the acidity are identical.

[1] *Bureau of Chem., Bull.* **66**, p. 52.

[2] Organic Analysis, p. 91.

That the percentage of acid in the juice affects this inversion is evident from a comparison of Nos. 100–102 (note discrepancy in 101); Nos. 110–112; and No. 150 with No. 151 and No. 153. In these instances the time is generally identical.

That the nature of the acid also affects somewhat the amount of inversion is illustrated by comparison of Nos. 151–152 with Nos. 153–154, the acid added to the two former being tartaric, and to the two latter citric.

The amount of this inversion that is desirable, in order to produce jellies of good texture, is a point more difficult to decide than the proportional amount of sugar to be used. Examination of the table shows that crystallization of cane-sugar occurred more readily generally, from the jellies in which inversion was least. However, in every case, this crystallization always occurred at the surface of the jellies and in none of the cases had any care been taken to protect these jellies from the air, as is ordinarily done, by paraffining the surfaces. Hence, there was every opportunity for evaporation from the surface of these jellies and the consequent formation of crystals.[1] That the sugar should not be boiled sufficiently long with the juice to insure practically complete inversion, is quite probable from the following experiments, as shown in Table VI.

Table VI.

Experiment No.	Kind of fruit.	Sp. gr. of juice.	% of acid in juice (calc. as H_2SO_4)	Wt of juice Grams	Sweetening constituent.	Proportion of sweetening constituent to juice by volume.	Wt. of sweetening constituent. Grams.	Time of boiling Min. Before adding sugar.	Time of boiling Min. After adding sugar.	Temp at which jelly-test was apparently observed.	Sp. gr. of hot jelly.	Texture of jelly.
160	Crab-apple	1.043	0.550	103	Cane sugar	¾ : 1	66.5	0	10	103°	1.27	Excellent
161	Crab-apple	1.043	0.550	103	Fructose	.....	66.5	0	10	103°	1.24	Syrup
162	Crab-apple	1.043	0.550	103 103	Equal wts. of d-glucose and fructose	.....	34.8 d-glucose 34.8 fructose	0	10	103°	1.26	Good (at first)
163	Crab-apple	1.043	0.550		Cane sugar	¾ : 1	66.5	8	2	103°	1.28	Excellent
143	Sour apple	1.041	0.257	103 103	Fructose	¾ : 1	62	0	20	104°	1.275	Syrup

That jellies can not be made through substituting fructose for cane-sugar is evident from Nos. 161 and 143, as only a thin syrup resulted in these cases. Corresponding experiments (not

[1] In other cases not cited in the table but within the writer's previous practical experience—cases in which such jellies as currant, red raspberry, and blackberry were paraffined as soon as they had set, no crystallization of cane sugar occurred even after a lapse of two years. In these cases a very small amount of inversion had probably taken place, since the sugar had been boiled with the juice not to exceed five minutes.

tabulated) substituting *d*-glucose for cane-sugar resulted apparently in a good firm jelly; however, *d*-glucose shortly began crystallizing from this jelly and soon could be seen throughout the mass. No. 162 in which equal weights of fructose and *d*-glucose were substituted for cane-sugar (representing a condition of complete inversion) resulted very similarly to the case in which *d*-glucose was used alone, *i. e.*, *d*-glucose crystallized out. No. 163 in which cane sugar was boiled with the juice for only two minutes finally showed evidence of cane-sugar crystals on the surface.

From all the foregoing results two things are apparently evident: First, some inversion of cane-sugar is desirable; second, an inversion approaching completeness is undesirable, see No. 162. So far as our researches now extend it seems better not to boil sugar and juice together from start to finish in jelly-making, but rather to add the sugar so that it may be boiled with the juice for a period not to exceed one-half the total time of cooking. However, we wish to investigate this point further.

Some experiments regarding excessive cooking of an over-diluted juice have been carried out. Results seem to show that the texture of the jelly may be greatly impaired in this way. This also demands further investigation.

V. Physical Constants.[1]—In connection with our work it seemed desirable to determine whether or not there is a boiling point or a definite specific gravity of the boiling jelly indicative of that condition at which a good jelly may be formed on cooling. Although it was impossible to determine these points with absolute accuracy yet reference to Tables V and VI shows a remarkable coincidence among these physical constants. Boiling points were observed by suspending a thermometer with the bulb in the boiling liquid, and specific gravities were observed by means of a hydrometer floated in the hot liquid which had been transferred with as great rapidity as possible to a glass cylinder previously heated with boiling water. That these boiling points and specific gravities coincide so nearly, even though we are dealing with different fruit-juices and very different proportions of sugar, is worthy of notice.

VI. Artificial Jelly.—That the essential substances for the formation of a jelly of good texture have been indicated in the foregoing is probable from the success attending the attempts to make jelly from an artificial fruit-juice. For this purpose it was necessary to isolate pectin. Pectin was obtained from crab-apple, grape, sweet apple, and peach juices. The isolation of this pectin was a difficult matter and the methods indicated by different experimenters[1] were tried. The following modification of their methods was finally adopted as the one giving the best results: a given volume of the cold, filtered (previously boiled) fruit-juice was added drop by drop by means of a separatory funnel to an equal volume of alcohol, stirring constantly; the mixture was allowed to stand over night in a cold place and then the precipitated jelly-like mass of pectin was separated from the liquid by filtering off through very fine cotton cloth stretched tightly over the mouth of a 4-liter jar. The liquid was worked out of the mass of pectin by means of a spatula. Repeated re-solution and re-precipitation of the pectin improv d its purity. The pectin so obtained was a very stable, nearly colorless, transparent solid, of insipid taste. Its principal reactions in solution were tried and correspond to those given by Braconnot, Fremy and others.

Jelly of excellent quality was easily made from this pectin by preparing a 1 per cent. solution of it in a 0.5 per cent. solution of tartaric acid, heating to boiling, then adding a 3/4 volume of sugar and boiling until the jelly-test was observed. The total time of boiling did not exceed 15 minutes. Jellies made as above were nearly colorless, but were excellent in texture and taste. When a few cc. of grape-juice were added to the pectin solution the color of the jellies was very pleasing. That these jellies were not made directly from fruit-juice would not be suspected from taste or texture. Jellies equally good were made in this way from the pectin from sweet apples, crab-apples, and peaches. This last fact would seem to indicate that the pectin of peaches does not differ materially, at least from a practical standpoint, from that of other jelly-making fruits.

It may be of interest to add that pectin was extracted from jelly (the jelly being previously dissolved in an equal volume of water) by the method used for extracting pectin from fruit juices. This pectin apparently corresponded in its physical and chemical characteristics with that extracted directly from fruit-juices. Good

[1] We understand that some work (unpublished) on these points, also on the relation between the proportion of sugar used and the amount of jelly produced, has already been done by Miss Jenny Snow, of the University of Chicago.

[1] Chodnew, *Ann.*, **48**, 56. Fremy, *Ibid.*, **64**, 383.

fruit jelly invariably gives the alcohol test for pectin. These facts would seem to indicate that pectin in the formation of jelly does not undergo any deep-seated change, but rather that the phenomenon of jelly-making is more nearly physical than chemical.

VII. Summary.—1. The essential constituents of a jelly-making fruit-juice are, first, pectin; second, acid.

2. A desirable accessory constituent is cane-sugar. Too much sugar is likely to be used in jelly-making with a consequent deterioration of the quality of the jelly. The amount of inversion preferably produced in this cane-sugar is yet undetermined.

3. Over-dilution of fruit-juice should be avoided, since this leads to the use of too much sugar; probably the extra boiling thus rendered necessary also impairs the texture of the jelly.

4. The physical constants of hot juice ready to jell on cooling are, substantially, boiling point 103° C., and specific gravity 1.28.

5. Jelly is readily made through boiling pectin with acid, water and sugar.

6. Jelly-making seems to consist in so controlling conditions by means of acid and sugar and boiling as to cause the pectin to be precipitated in a continuous mass throughout the volume allotted to it.

Research Laboratory of the
Department of Household Science,
University of Illinois.

[Contribution from the Bureau of Chemistry, Department of Agriculture.]

A STUDY OF THE FATTY ACIDS OF FISH OILS.

By L. M. Tolman

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This study was undertaken several years ago in connection with an investigation of the cod-liver oils and related fish-liver oils, part of the results of this work being published in the *Journal of the American Chemical Society*, **28,** 387–395 (1906). The oils used in this study were prepared for us by the Bureau of Fisheries, Department of Commerce and Labor, so that their exact history and purity were known. The oils selected for this especial work were a sample of Norwegian cod-liver oil, American cod-liver oil, a pollock-liver oil, a hake-liver oil, a ling-liver oil, a dog-fish liver oil, a trout-liver oil and a seal blubber oil. These were chosen as they formed a series of oils representing fish closely related to the cod fish widely separated from the cod, and a fresh water fish whose habits of food were entirely different, while the sample of seal blubber oil gave an oil from a warm-blooded animal which largely subsists upon fish. In addition, a sample of linseed oil and one of corn oil were examined in order that a comparison could be made between the highly saturated vegetable oils and the highly unsaturated fish oils. The following table (I) gives a description and analysis of the oils enumerated:

Table I.—Description and Analyses of Fish Oils.

Description of sample.	Sp. gr. 15.6° C.	Index of refraction.	Iodin number.	Hexa-bromid. Per cent.	Saponification No.	Solid acids. Per cent.	Free acids. Per cent.	Unsaponifiable matter. Per cent.
2447 Cod.......	0.9265	1.4810	165.7	46.6	178.1	5.70	0.47	....
15600 Cod.......	0.9274	1.4805	168.0	34.0	188.6	15.55	0.28	0.91
14261 Pollock	0.9245	1.4795	150.9	42.7	...	15.99	0.95	....
14304 Hake ...	0.9254	1.4812	158.2	30.3	178.1	13.58	0.56	0.76
11556 Ling......	0.9224	1.4784	143.4	30.2	183.1	14.42	0.91	....
15604 Dog fish...	0.9220	1.4786	153.3	37.2	180.3	18.52	0.65	3.20
16780 Trout ...	0.9275	1.4801	154.8	35.1	189.4	7.01	1.69	....
15608 Seal.......	0.9246	1.4776	143.8	19.5	191.1	9.96	0.64	0.13

These oils, as will be seen from the results given in this table, do not show a very wide variation in the chemical and physical characteristics. Considering the chemical analysis alone, all of the oils would come within the limits allowed or found in our experiments for cod-liver oil, except the seal and dog fish oils, which are somewhat different in the amount of unsaponifiable matter; and and yet it would be difficult to select a more varied lot of oils as far as the source is concerned. In the study of the unsaturated acids, the halogen compounds, especially the bromin compounds, were used as the basis for the separation of the unsaturated fatty acids. After a careful consideration of the various methods, and after experimenting to a considerable extent with the oxidation with dilute permanganate, as suggested by Hazura, it was decided that the formation of the insoluble brominated acids gave more information as to the composition of the fatty acids than any other of the methods which have been applied. As the methods used in separating the saturated and unsaturated acids and the determination of the iodin numbers are in a sense empirical methods, it is necessary at least to name them, and in some cases to give the method employed in detail.

The Hanus method was used for all of the iodin absorption determinations and accounts for the fact that the results on this determination are somewhat higher than the older figures which are

based on the Hübl method, but the range of variation should not be any greater on this account, as the Hanus method gives almost uniformly slightly higher results. The iodin number of the fatty acids were all calculated on the basis that the oil would contain 95.5 per cent. of insoluble acids, which is near enough to the truth and probably more accurate than a determination would be on oils which are so easily changed by oxidation. The iodin numbers of the liquid fatty acids can be calculated, after the determination of the saturated fatty acids had been made, only a simple calculation being required. As the saturated fatty acids had, as a rule, an iodin absorption figure of from eight to ten, due to the presence of a small amount of unsaturated acids, it was always determined and corrected for in determining the true per cent. of saturated fatty acids, calculating it as oleic acid, although it may be some other one of the oleic acid series. However, the iodin numbers of all of the acids of the oleic series are so close together that it makes very little difference which is taken as the basis for the correction. This gives what has been termed the true iodin number of an oil and the results by calculation are closer to the true results than a determination would be unless the preparation of the fatty acids was so conducted that the oxidizing effects of the air were excluded in all of the operations, which is very difficult, indeed well-nigh impossible. On the other hand, the calculations depend on the determination of the iodin number of the oil itself, which can be made with great accuracy, and on the determination of the saturated fatty acids, which is satisfactory and must be employed if the liquid acids are to be prepared for direct determinations, so that the same errors will occur in either case.

The methods used for the separation and estimation of the bromin compounds were essentially those proposed by Hazura, but the mechanical details were so modified as to greatly assist in the manipulation and will be described in some detail, especially on account of the paper by Proctor and Bennet[1] in which they described the obstacles encountered in handling the method, and the way in which they tried to overcome these difficulties by changing the method entirely, using a different solvent. From the experience of the writer, this appears to be entirely unnecessary when using the method employed by him for the last two years on this study.

[1] *Jour. Soc. Chem. Ind.*, **25**, 798 (1906).

The difficulty of handling the precipitate is the chief source of trouble, due to the volatility of the solvent, and also to the peculiar gummy consistency of the precipitate, which soon clogs any kind of filter and prevents filtration. Hehner and Mitchel[1] tried the use of a linen filter tied over the end of a glass tube, drawing off the supernatant liquor by means of suction, but as Proctor and Bennet have shown, and any one who has tried the method finds at once, this is very unsatisfactory and inaccurate, and gives a very poor separation. In order to get around this trouble, the writer resorted to the use of the centrifuge and found that it gave quick and satisfactory results. The precipitate, being much heavier than the solvent, readily separates, and on account of its peculiar consistency, packs in the bottom of the centrifuge tube in such a manner that the supernatant liquor can be easily and accurately decanted without any loss. The determination was made in glass stoppered weighing bottles about six inches high and one inch in diameter, which had flat bottoms and weighed only about thirty grams.

The method employed in making the bromin precipitate was to dissolve the oil or fatty acid in absolute ether, acidify with acetic acid, cool in a bath of ice-water, and add an excess of bromin so as to insure complete bromination. Allow the tube to stand for half an hour in ice-water, and then place it in the centrifuge and whirl at about 1200 revolutions per minute for two to three minutes. Dry the weighing tubes, weigh the proper amount of oil or fatty acid into them, add 25 cc. of absolute ether and a drop of acetic acid, cool in ice-water to 2°–3° C., and add the bromin drop by drop until there is a considerable excess as shown by the color of the solution. The solution should be stirred constantly during the addition of the bromin, which must be added very slowly, as a large amount of heat is generated in this reaction, and the ether will boil violently if the bromin is added too rapidly. Especially is this precaution necessary when brominating the fatty acids which react very violently with the bromin. After the tubes have stood for the necessary thirty minutes, they are placed in the centrifuge in special holders, which keep them from shifting about, and whirled. Then the supernatant liquid is decanted, which can be done very completely. Before decanting, it was the practice to put the tubes back in the ice-water to cool down again so as to throw out

[1] *Analyst*, **1898**, 313

any bromids that had been dissolved, but this was found to be practically unnecessary, as the ether solution remained clear. This shows that the precipitate does not dissolve in the time taken to centrifuge it, although the temperature rises somewhat. Ten cubic centimeters of cold ether are added and the residue in the bottom of the tube stirred with a glass rod so as to thoroughly wash out the excess of bromin. The tubes are again cooled in the bath of ice water and again whirled and decanted. Another washing like this will completely remove the excess of bromine and leave a pure white precipitate in the bottom of the tube, which is allowed to stand until the ether has evaporated, and is then dried in a water bath for thirty minutes and weighed. The bromids prepared in this way are nearly white with a slight amber color, and have a very uniform content of bromin.

The advantages of this method can easily be seen. The oil or fatty acids and the final product are weighed in the same bottle, so that there are no losses by transfer, there is no filtration with evaporation of the volatile solvent and difficulties of washing the precipitate free from the other bromids which are thrown out of the solution when the solvent evaporates; but the chief advantage is the rapidity with which the determination can be carried out which makes possible its application in technical analysis. This method can be applied to the determination of the tetrabromids as suggested by Farnsteiner, using petroleum ether as the solvent instead of sulphuric ether, but carrying out the separation in the same manner as before.

Determination of bromin.—The determination of bromin was made in two ways, both of which gave satisfactory results. The first was by fusion with calcium oxid and sodium carbonate by placing the material in the bottom of a small crucible, filling it with the mixture, inverting the crucible in a large crucible, and then filling the space between the walls of the two vessels with the fusion mixture. The bottom of the outside crucible is then heated. This method insures holding all of the bromin and very satisfactory results were obtained. The second method, and the one found to be most satisfactory and most rapid, was burning with sodium peroxid, as suggested by Pringsheim[1] in an iron crucible. This method depends on making a mixture of the material to be burned with sodium peroxid and sugar, the proportions depending on the percentage of bromin in the material used. Instead of an iron crucible, as suggested by Pringsheim, the writer used the bomb of a Parr calorimeter, placing it in a pail of cold water and ignited the mixture with a red hot piece of iron wire. The combustion was always complete. Any bromates formed were reduced by adding a few cubic centimeters of a saturated solution of sodium sulphite to the solution before making acid with sulphuric acid. The precipitation of the silver salt of bromin is made from a solution very strongly acid with nitric acid to prevent the precipitation of silver sulphate. This method is very rapid, gives very accurate results, and was used for all of the determinations of bromin.

[1] *Amer. Chem. Jour.*, **31**, 386 (1904).

The amounts of fatty acids in the various bromin precipitates were calculated from the weight of the precipitate and the percentage of bromin found in them. The iodin number of these fatty acids was calculated from these results from the ratio between bromin and iodin.

The saturated fatty acids were determined by the lead salt ether method, and the iodin number was determined so that a correction could be made. This figure was generally found to be from 8 to 10, about the same as is found in olive and other vegetable oils, which throws doubt on the claim that there is present in fish oils an unsaturated fatty acid, having a lead salt insoluble in ether. The percentage of unsaturated fatty acids was calculated from the percentage of total fatty acids taken as 95, and the amount of saturated acids as determined.

The oxidation methods were practically those of Hazura, except that the oxidation was made in a more dilute solution, and this was kept at a low temperature by means of ice, as was suggested by Heyerdahl, higher yields being obtained. But even following this procedure the writer was not able to obtain any oxidation products of the higher unsaturated acids, thus confirming the results of Heyerdahl and showing that these acids do not conform to Hazura's rule of forming hydroxy acids, as do the higher unsaturated acids of the vegetable oils like linseed oil, showing that these acids are of a different series.

Table II gives the results of the study of the bromin compounds of the glycerids and of the fatty acids of the various oils studied. Results on linseed and corn oil are also included, to furnish

a comparison of the fatty acids from vegetable oils and from the fish-liver oil.

Before discussing the analytical results, an explanation of the various headings given in Table II should be made. The first column gives the iodin number by the Hanus method; the second column, the iodin number of the fatty acids calculated from the previous determination; the third column, the saturated fatty acids, or the solid fatty acids as determined by the lead salt ether method. The total liquid acids or the unsaturated acids, given in the fourth column, are obtained by taking the difference between the saturated fatty acids and 100. The next two columns, headed the "brominated fatty acids insoluble in ether," show the fatty acids which are precipitated when the total fatty acids are dissolved in ordinary ether and brominated, the column labeled "per cent." unsaturated acids soluble in petroleum ether," were calculated from the amount of saturated fatty acids, the iodin number of the fatty acids and the per cent. of fatty acids thrown down in petroleum ether by means of bromin. It is not necessary to go into this calculation as it is a simple one; it simply shows in a general way that there is a very large amount of unsaturated fatty acids with a comparatively low iodin number.

Under the next general heading are the bromids precipitated from ether and petroleum ether solution, when the glycerids or oils themselves are brominated. The columns headed "per cent." under this general heading give the percentage of the amount of oil taken originally that the actual weight of bromin precipitate represents. The columns headed "per cent. of bromin" of course need no explanation.

TABLE II.—COMPOSITION OF THE FATTY ACIDS.

Serial No.	Description.	Iodin No	Iodin No. of fatty acids.	Saturated acids. Per cent.	Total liquid acids. Per cent	Brominated fatty acids insoluble in ether.		Brominated fatty acids insoluble in petroleum ether.		Brominated unsaturated acids soluble in petroleum ether.		Glycerids. Bromids precipitated from ether.		Glycerids. Bromids precipitated from petroleum ether.		Fatty acids. Bromids precipitated from ether.		Fatty acids. Bromids precipitated from petroleum ether.	
						Per cent.	Iodin No.	Per cent.	Iodin No.	Per cent.	Iodin No.	Per cent.	Per cent. Bromin.	Per cent.	Per cent. Bromin.	Per cent.	Per cent. Bromin.	Per cent.	Per cent. Bromin.
2447	Cod-liver oil...	165.7	173.6	5.70	94.30	...	...	36.00	331.5	58.30	93.1	46.60	57.65	...	...	35.76	...	112.30	67.68
15600	Cod-liver oil...	168.0	175 9	15.55	84.45	11.08	358.0	28.58	356.0	55.87	132.7	34.08	59.20	95.60	58.05	36.12	69.35	93.82	68.50
15608	Seal oil.......	143.8	150.6	9.96	90.04	8.68	363.5	22.14	322.5	67.90	116.6	19.57	60.05	78.75	58.24	28.77	69.83	67.06	67.20
15604	Dog-fish liver oil..........	153.3	160.5	18.52	81.48	8.28	340.5	30.09	318.0	51.39	126.1	37.24	...	88.65	58.88	26.08	68.25	90.50	66.75
14261	Pollock oil.....	150.9	158.0	15.99	84.01	8.55	362.0	23.19	344.5	60.82	128.4	42.76	58.85	92.50	57.90	27.99	69.45	73.62	68.50
14304	Hake oil.......	152.8	159.8	13.58	86.42	7.83	381.2	22.95	347.7	63.47	126.0	30.32	58.10	...	...	26.68	70.65	73.32	68.70
14278	Haddock oil...	170.5	178.5	13.11	86.89	10.83	350.4	34.96	326.1	51.93	124.2	57.54	58.30	...	...	34.78	68.95	105.30	66.80
11556	Ling oil	143.4	150.2	14.42	85.58	7.27	361.1	23 89	349.0	61.69	108.3	30.28	58.10	...	...	23.84	69.55	76.54	68.80
16780	Lake trout liver oil..........	154.8	162.1	7.01	92.99	8.29	351.5	24.08	321.3	68.92	123.0	35.10	59.74	...	...	26.74	69.00	73.08	67.05
	Linseed oil....	...	...	...	...	13.57	262.7	34.61	212.3	...	...	28 82	56 63	...	...	36.04	62.35	81.06	57.27
	Corn oil.......	122.7	128.5	...	...	...	...	12.86	186.0	...	...	...	...	...	...	slight precipitate	...	27.96	53.70

being the actual percentage of fatty acids precipitated by this method, while the iodin number is the percentage of iodin absorbed by these fatty acids as calculated from the percentage of bromin found in the bromin precipitate. All of the results have been calculated to the basis of iodin rather than bromin, so that these figures can be compared with the iodin number of the oil and of the fatty acids. The next column headed "brominated fatty acids insoluble in petroleum ether" shows the amount of fatty acids precipitated when petroleum ether is used as a solvent rather than ordinary ether, and the columns under this general heading, "per cent." and "iodin number," have the same significance as the two preceding columns.

The figures under the next heading, "brominated

The next general heading, "fatty acids—bromids precipitated from ether and petroleum ether," means that in these determinations the fatty acids were used instead of the glycerids, the columns headed "per cent." being the same as under glycerids, more than 100 per cent. obtained in some cases, because the bromin precipitate obtained in the determination weighed more than the amount of fatty acids taken originally.

A detailed discussion of one of the analyses will explain all, so the one that is most complete will be considered. Sample 15600, a cod-liver oil, will serve as a typical case. The iodin number of the oil is 168.0, and the iodin number of the fatty acids is 175.9. The iodin number of the fatty acids precipitated from ether by bromin is 358.0,

which compared with the same figure for the fatty acids of linseed oil, namely 262.7, shows at once a great difference between the fatty acids of cod-liver oil and the linolenic acid of linseed oil, the latter being the most unsaturated acid known to occur in any oil of the vegetable or animal kingdom, considering land animals only. This figure shows that this fatty acid must have eight unsaturated bonds to take up iodin, which confirms the work of Heyerdahl and Bull as to the presence of the highly unsaturated acids in fish-liver oils. The fact that theory would require an iodin number of about 387 for a pure acid, shows that this precipitate is a mixture of the acids requiring eight atoms of iodin with acids requiring six or less. There are 11.08 per cent. of fatty acids with this high iodin number. By using petroleum ether as a solvent a much larger amount of bromids are precipitated, representing about 28.58 per cent. of the total fatty acids having an iodin number of 356.0, which is only a little lower than the iodin number of the fatty acids precipitated from ether, and these are also undoubtedly mixtures of the higher and lower unsaturated fatty acids.

The bromids are somewhat different in consistency, the ether precipitate being amber colored and very brittle, while the precipitate from petroleum ether is dark colored and a little gummy. Figuring on the basis that the fatty acids of eight unsaturated bonds have an iodin number of 387 and those of six unsaturated bonds have an iodin number of 274, the mixed fatty acids represented by the iodin number of 358 is made up of a mixture of about 75 per cent. of the eight unsaturated bond acids, and 25 per cent. of the lower unsaturated fatty acids and the precipitate from petroleum ether maintains about the same ratio, showing that all of the octobromids are not thrown down in the ether solution. This leaves 84.45 per cent. of unsaturated fatty acids having an iodin number of 132.7, evidently made up of a mixture of acids of the oleic series and the linolic series, which shows that there is present in these fish oils a complete series of fatty acids from those with two unsaturated bonds to acids with eight unsaturated bonds. That they are quite different from the series present in linseed oil is shown by a number of different reactions—the solubility of the bromids in ether and petroleum ether, the melting point of the bromids, and the action of the fatty acids toward dilute permanganate, these acids not forming the hydroxy-acids as do the fatty acids of linseed oil, but being apparently completely oxidized, while the acids with two unsaturated bonds are the only ones of the series to form hydroxy acids.

Treating the glycerids in the same manner as the fatty acids (that is, dissolving in ether and precipitating with bromin, collecting the bromids and analyzing), we find a very peculiar condition. The iodin number of the precipitated glycerids from ether is only 229, which shows at once that it cannot be the triglycerid of the fatty acid with eight unsaturated bonds, as that would have an iodin number of 369.9; in fact this figure is lower than the figure for the triglycerid of the acids with six unsaturated bonds which would be 262.15, all of which goes to show that the glycerid which is precipitated by bromin under these circumstances is a mixed glycerid and must be made up of at least one acid radical of the very unsaturated acid and one radical of the saturated acids or the acids with two unsaturated bonds; possibly the third acid radical is still different, at least there is very good evidence that here we have a combination of glycerin with at least two different fatty acid radicals, and perhaps three. This brings the iodin number of the precipitate from ether for the fish-liver oils and the linseed oil quite close together, the linseed oil having 207.0 as compared with 229.9 for the cod-liver oil, a very slight disparity considering the difference between the respective iodin numbers of the bromin precipitated fatty acids, which are 358 for fish oils and 262 for linseed oil. This only emphasizes the difference in the glycerids precipitated from the two classes of oils. This high iodin number appears to be characteristic of these fish oils and the related oils, such as those from the seal and whale and also is found for the trout liver, a fish with entirely different food and living in fresh water.

A general consideration of the figures in this table shows the remarkable similarity of the oils from the various fish including the seal oil; in all of these the same series of fatty acids seems to be present, and in about the same proportion, which makes the oils very similar. This similarity holds true also as to other properties of the oils and in the changes that take place on being exposed to air. In fact, there seems to be little doubt that these oils have about the same value, and the recent work of Bull confirms the great similarity among the oils from various fish and from animals like the seal.

In conclusion it appears that the results of this work have (1) developed a method for the determination of hexabromid, or bromin precipitate as it should be called, which is satisfactory and easy to manipulate; (2) that little, if any, information can be obtained by the oxidation of these fatty acids with permanganate, as apparently they are so readily and completely oxidized that no hydroxy acids are formed with the highly unsaturated members of the group; (3) that the presence of mixed glycerids of undetermined composition, is proven; (4) that the unsaturated fatty acids present in the fish oils belong to a series entirely different from any that are known at present in any of the vegetable or animal (land animals) oils as yet studied; (5) that the fish and blubber oils are remarkably alike in the composition of the unsaturated fatty acids and mixed glycerids present; (6) that the oil from animals living on fish is remarkably similar to fish oil in the composition of the unsaturated fatty acids and the mixed glycerids; (7) that even the oils of fresh water fish like the trout, living on entirely different foods, are remarkably similar to the oils from the cod and other similar salt water fish; (8) that these oils present a very interesting field for investigation in further separation and study of a very peculiar series of fatty acids, both along the line of preparing hydroxy acids with other oxidizing agents less active than permanganate, and in further study of the bromin compounds, as in my opinion the *special value* of the cod-liver oil in a medicinal way must be in these extremely easily oxidized series of fatty acids.

THE RELATION BETWEEN THE TEMPERATURE OF KEROSENE AND THE EXPLOSION PRESSURE OF THE SUPERNATANT MIXTURE OF AIR AND VAPOR.

By W. P. Bradley and C. F. Hale.

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The testing of kerosene oil, so far as it concerns the safety of the oil as an illuminant, is based upon the relation of temperature to its rate of vaporization. The rate of vaporization is judged by the result of ignition tests. These tests are of two sorts. In one, which is called the fire-test, a determination is made of the lowest temperature at which the oil will give off vapor fast enough to support a permanent flame when ignited. In the other, which is called the flash-test, the saftey of the oil is judged by the temperature at which it first vaporizes sufficiently to form with the supernatant air a mixture rich enough to ignite at all.

The fire-point is often spoken of erroneously as the temperature at which the oil itself takes fire. But it is hardly necessary to say that the oil, as liquid, never burns; that all flame is gas or vapor flame; and that what burns on the surface of the oil, at any time and at any temperature, is only the vapor of the oil.

The danger attendant upon the use of illuminating oil is threefold: (1) danger from conflagration when the oil is in bulk; (2) danger from conflagration when the oil is spilled; (3) danger from explosion.

Those who advocate the fire-test emphasize the danger from conflagration if oil is spilled in any way. They appear to ignore the danger from explosion, as practically non-existent.

Those who advocate the flash-test, while admitting the danger from conflagration, emphasize the earlier danger arising from the presence, *in the bowl of the lamp*, of explosive mixtures of inflammable vapor and air, which, if ignited in any way, might burst the lamp, scatter the oil, and so induce conflagration, in addition to the more direct damage arising from the explosion itself.

Now it may readily be admitted that a liquid whose vapor will catch fire from a spark or match, at such temperatures as are prevalent within dwellings or without, is a dangerous liquid, whatever its name or use may be, and that a grade of kerosene which will not so ignite is safer. There can be no question that a merchantable kerosene should be required to pass a fire-test of considerably higher temperature than any which will normally prevail during its use as an illuminant. A body of oil which will stand such a test will not only not ignite at ordinary temperatures, but it will extinguish a spark or match as effectively as water does. All grades of kerosene now on the market will do as much as this.

However, danger from conflagration depends upon other factors than that of temperature, and particularly upon one, namely, the presence of some kind of absorbent material, whether itself inflammable or not, which can perform the functions of a wick. Oil which will extinguish a flame, in bulk, will take fire very easily and burn freely, if soaked into textile material. Indeed, within very wide limits it may be said that the inflam-

mability of kerosene which has fallen upon, and has soaked into, a carpet or upholstery has no relationship at all to the inflammability of the same oil in bulk. Whether a conflagration occurs in such a case depends scarcely at all on the grade of the oil, as determined by fire-tests or by flash-tests, but solely on the accidental circumstance that a flame does or does not come into contact with it. Moreover, as a grade of kerosene which would not take fire under these circumstances would not ignite at the wick of a lamp either, it is clearly impossible to avoid this particular species of danger by any test at all. A fire-test, therefore, simply guarantees against danger from conflagration while the oil is in bulk, and while it is kept at temperatures below that of the test. It does not, and from the nature of the case cannot, guarantee against danger from conflagration, after the oil is spilled.

The third danger attendant upon the use of kerosene as an illuminant will be readily appreciated in this day of gas engines and gasolene engines. Indeed, explosive mixtures of air and the vapor of kerosene itself are being used more and more to drive engines of the explosive type. Danger from explosion is always present where inflammable vapors and air are mixed together. This condition may arise in the bowl of any lamp. Above the liquid kerosene there is always kerosene vapor, and there is always air. The proportions of vapor and air depend upon the temperature of the oil. There is more vapor at a high temperature and less at a lower one.

Now it is a well-known fact that such a mixture cannot explode if it is too poor in vapor, or too rich. The proportions must lie within certain maximum and minimum limits. Even within these limits, there can be no explosion, unless a spark or flame comes in contact with the mixture. Near the maximum, and near the minimum limit, the explosion is feeble. Explosion of greatest violence occurs when the proportions are such that the amount of air present is exactly right to burn the vapor completely. An excess of either air or vapor serves as a cushion to moderate the force of whatever explosion does occur. And it is well known that the force of the explosion drops off very rapidly indeed as a result of even moderate departure from the correct proportions.

Now the minimum limit in the matter of proportions, which is the beginning of danger from explosion when the mixture is ignited in confinement, is precisely the point which is approximately indicated by the flash-point of the oil, as observed in the so-called closed cup. And as the flash-point of an oil in the closed cup is from thirty to forty-five degrees[1] lower than the fire-point, depending on the degree of protection from drafts afforded by the various styles of cup, if the flash-point is higher than any temperature to which the oil is likely to be exposed during normal use, it is clear that danger from conflagration in bulk, as well as danger from explosion, will be eliminated. When these two dangers are avoided, all has been done which can be done by the legal establishment of standards, for danger from oil which is spilled can never be eliminated, as has been said, if the oil is to burn at all in the lamp.

There are several ways in which an explosive mixture in the bowl of a lamp might become ignited, but probably the one of most frequent occurrence arises from the use of a wick too small for the burner, whereby communication is afforded between the mixture and the flame. Experimental evidence on this point has been furnished by Kast and Rose[2] who found that with a wick which did not fit the burner closely an explosion always occurred when the temperature of the oil in the bowl of the lamp became sufficiently high.

Now, it should be noted that the conditions under which flash-tests are made are of great importance, if the tests are to serve as a guarantee of safety from explosion.

Two general types of apparatus, designated respectively as the *open* and the *closed* cups, are used to determine flash-points. In the closed cup an attempt is made to proximate the conditions under which vaporization takes place, to those which obtain in the bowl of a lamp. The space above the oil is closed in by a cover, except for a small aperture provided for the introduction of the ignition torch. The conditions in the case of the open cup are different. Here the oil vaporizes into the open air, which is always more or less disturbed by currents which disseminate the vapor, and which militate against the formation of the flash mixture at all. It is not surprising therefore that the flash-point of a given sample of oil is invariably several degrees higher in the

[1] For the sake of easier comparison with the legal standards which prevail in this country, all the temperatures given in this paper are those of the Fahrenheit scale, in the first instance. The corresponding values according to the centigrade scale are also given.

[2] *Journal für Gasbeleuchtung*, **39**, 348–351, 364–368; and *Central-Blatt*, **1896**, II, 142 and 220.

open cup than in the closed cup,[1] for the rate of vaporization must be more rapid in the former before a sufficiently rich mixture can be obtained.

It is evident that the fire-test, involving as it does continuous combustion of vapor, can never be made at all except in a cup which is open, for the time at least. But here again it makes a difference of about the same number of degrees whether the oil fills the cup nearly to the rim, as is customary in the usual forms of "open" cup, or whether the surface is protected somewhat from drafts by an extension of the rim upward, as in one form of the closed cup, the Elliott.

Taking the Tagliabue open cup and the Elliott closed cup as a basis for discussion, we have no less than four tests for one and the same oil. Each of these tests is spaced from its neighbor by approximately fifteen degrees. The following table illustrates this by the use of two general samples of oil, both purchased in open market, and representing respectively a rather low-grade, and a rather high-grade kerosene.[2] Portions of these same samples were used in the explosion tests which follow, and will be referred to later.

TABLE I.—COMPARISON OF FLASH- AND FIRE-TESTS.

Sample.	Elliott flash. Fah.	Tagliabue flash. Fah.	Elliott fire. Fah.	Tagliabue fire. Fah.
1	112 (44.5)	127 (52.8)	141 (60.5)	158 (70,
1 A	114 (45 5)	128 (53.4)	142 (61)	159 (70 5)
1 B	114 (45.5)	129 (53 9)	142 (61)	158 (70)
2	88 (31)	103 (39.5)	114 (45.5)	126 (52.2)
2 A	89 (31.7)	104 (40)	114 (45.5)	128 (53.4)
2 B	89 (31.7)	104 (40)	114 (45.5)	128 (53.4)

The danger which ensues when a mixture of inflammable vapor and air becomes ignited is due of course to the pressure which is exerted at the moment of explosion upon the walls of the containing vessel. The quantitative relation between this pressure and the temperature of the oil at the moment of explosion seems never to have been determined experimentally, but qualitative results have been reported by several writers. Kast and Rose[3] withdrew samples of the air-vapor mixture from the bowl of a lamp at intervals, after certain measured portions of the oil had burned, and ignited them in a pipette. The pressures, however, were not measured. Newbury and Cutter[1] separated the constituents of kerosene by fractionation and determined the temperatures at which the different fractions would give explosive mixtures with the amount of air necessary for the complete combustion of the sample. The magnitude of the pressures is not recorded beyond the statement that they were violent.

In the hope of throwing some light on this point the present investigation was undertaken.

Method of Experimentation.—In general, the method of experimentation consisted in the measurement of the pressures developed by the explosion of mixtures of air and vapor, obtained by passing air through oil heated to different temperatures. The apparatus employed is shown diagrammatically in Fig. 1. It is composed essentially of two parts—a stout brass cylinder, A, in which the explosion takes place, and a pressure indicator, B, of the type commonly used in the measurement of engine horse-power. The explosion cylinder was 13.5 cm. from dome to dome, 7.5 cm. in diameter, and had a capacity of 560 cc. On the left is a small copper tube I, of 3.2 mm. internal diameter, which is bent at its lower end into a small circle. The upper side of the circular portion is drilled with small holes. This tube serves for introducing the air, and it can be closed externally by the cock S. The straight tube T at the right is closed at its lower end, and contains a small amount of water in which the thermometer for measuring the temperature of the oil is immersed. At C is a stout copper wire insulated by a sheath of wood, and held in place by a brass supporting tube which is attached to the cylinder by a short coupling. The wire serves as one terminal for producing a make and break-spark, and it can be rotated within its sheath so as to bring it into contact with the inside of the neck of the cylinder, which is the other terminal of the circuit. The spark serves to ignite the mixture.

The neck of the cylinder is threaded to receive the short connection N, and is provided with a side tube, O, which permits the escape of the excess vapor and air as well as that of the products of combustion when a new charge of air is being admitted through I. When O is not in use, it is closed by the stopcock S′. To the upper part of N the indicator is attached, as shown.

Two other experimental details must be mentioned. First, provision must be made for the regulation of the air supply, and second, for the

[1] About fifteen degrees higher, for instance, in the Tagliabue open cup than in the Elliott closed cup.

[2] On Jan. 8, 1906, a lamp explosion of considerable violence occurred in this city, resulting in loss of life. Oil No. 1 was the grade which had been in use up to that time. Following that event, and pending revised legislation on the subject, oil of the grade of Sample No. 2 was used.

[3] *Loc. cit.*

[1] *American Chemical Journal*, **10**, 356–362 (1888).

control of the temperature. The arrangements for these will be clear from Fig. 2. The explosion cylinder is placed in a water bath, H, heated by a Bunsen burner, uniformity of temperature being secured by a wire stirrer. The air supply is de-

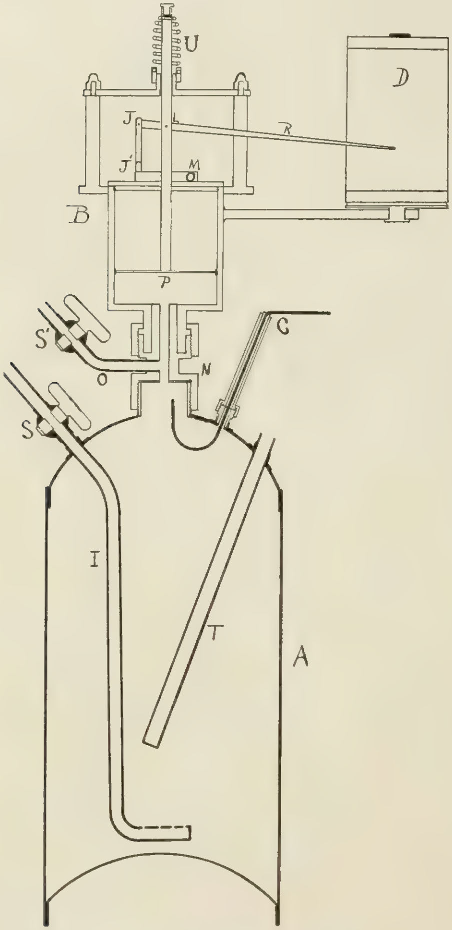


Fig. 1.

livered from the gas washing bottle A, whose air is displaced by water from the reservoir R. In all the experiments the water was allowed to flow into the wash bottle up to a certain point in its neck. Uniformity of speed in the delivery of the air supply was secured by a constant level of water in the reservoir.

Each sample of oil was first examined with reference to its two flash-points and its two fire-points, by the use of the Elliott and the Tagliabue testers. Another portion of the sample was then introduced into the cylinder. This portion, amounting to 390 cc., occupied rather more than two-thirds of the total volume of the cylinder, giving a condition comparable with that in a lamp which has been burning for some time. The indicator was then attached, and the cylinder was placed in the water bath. The temperature of the oil having been made constant at a point about one degree lower than the Elliott flash-point, the cocks S (Fig. 1) and P (Fig. 2) were opened and a charge of air allowed to bubble through the oil, escaping so far as necessary through S′. Then, with S and S′ closed, the mixture was exploded. The

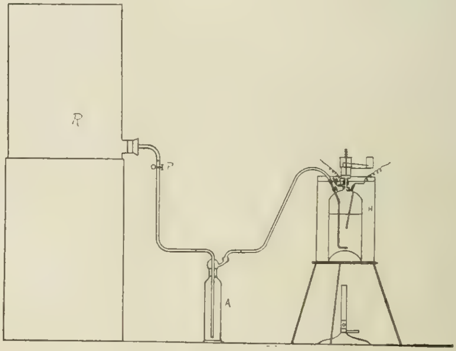


Fig. 2.

first explosion at each temperature was rejected as abnormal. The pressure obtained was higher than any subsequent explosion at the same temperature, probably owing to the excess of vapor formed during the heating process. After the first, the explosions were remarkably concordant.

Immediately after each explosion, the thermometer in T showed a rapid rise of about two degrees, after which the temperature fell in a short time to its former value. After thermal equilibrium was reached, a series of three explosions was made for each temperature, using a new charge of air in every instance. Each of these series was spaced from the next by about five degrees, and the total range of temperature covered with a given sample extended from that at which the mixture was too poor to explode, to that at which it was too rich.

Fig. 3 gives an idea of the appearance of the indicator card after a complete set of explosions.

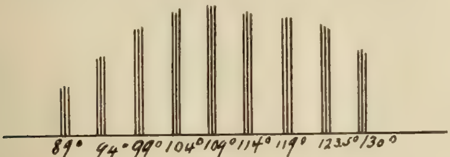


Fig. 3.

At the conclusion of an experiment, the cylinder was removed from the bath and quickly cooled to the temperature of the room, by immersion in running water. The oil was then removed, and transferred to the testers for a determination of the flash-points and fire-points as before.

Some preliminary observations had shown that the test-points of kerosene could be considerably raised by a small amount of evaporation,[1] and it was feared that such might be the case during these explosion tests. It was found, however, that the flash-point in the closed cup, the test which could be made with the greatest accuracy, was never raised more than two degrees, even in the case of the oil of greatest volatility. It is evident then that the explosion pressures obtained are fairly representative of the pressures which might result if the oil were to be heated at once to each of the temperatures employed, without previous explosions. Whatever change does occur in the nature of the oil by gradual evaporation during the determination of a set of explosion pressures, results in shifting the maximum pressure towards a region of higher temperature, and thus makes the indicated danger less than it really is in a fresh sample. The results follow.

Table I.—Temperatures and average explosion pressures obtained with kerosene oil, sample No. 1—Flash-point: Elliott, 112° F.; Tagliabue, 127° F. Fire-point: Elliott, 141° F.; Tagliabue, 158° F.

No. 1 A.		No 1 B.	
Temperature. Fah.	Pressure. Lbs.	Temperature. Fah.	Pressure. Lbs.
109	3	114	33
115	38	120	49
120	48	126	62
125	58	130	68
131	68	134	69
134	69	138	68.5
140	68	142	68
145	62	147	63
150	57	154	52
160	40	164	33
		169	5

[1] Compare also Newbury and Cutter, *Loc. cit.*

The test-points of this sample, after the explosions, were: No. 1A—Flash-point: Elliott, 114° F.; Tagliabue, 128° F. Fire-point: Elliott, 142° F.; Tagliabue, 159° F. No. 1B—Flash-point: Elliott, 114° F.; Tagliabue, 129° F. Fire-point: Elliott, 142° F.; Tagliabue, 158° F.

Table II.—Temperatures and average explosion pressures obtained with kerosene oil, sample No. 2.—Flash-point: Elliott, 88° F.; Tagliabue, 103° F. Fire-point: Elliott, 114° F.; Tagliabue, 126° F.

No 2 A		No 2 B.	
Temperature Fah	Pressure Lbs	Temperature. Fah.	Pressure. Lbs.
87.5	13	89	23
90	35.5	94	43
95	47	99	56.5
100	59	104	66
105	64	109	68.5
110	71	114	69.5
115	70	119	66
120	66	123.5	62
125	61	130	49
130	48	134.5	No explos.
135	No explos.		

The test-points of this sample after the explosions were: No. 2A--Flash-point: Elliott, 89° F.; Tagliabue, 104° F. Fire-point: Elliott, 114° F.; Tagliabue, 128° F. No 2B—Flash-point: Elliott, 89° F.; Tagliabue, 104° F. Fire-point: Elliott, 114° F.; Tagliabue, 128° F.

The data contained in these tables, together with the flash- and fire-points, are shown graphically in Figs. 4 and 5.

In their general form these curves are very similar. Their crests for instance lie at almost the same pressure. It is interesting to note, however, that the range of temperature covered by the high-grade oil is about sixty degrees, while that of the low-grade oil is only fifty. The latter oil gave no explosions at all beyond 130°, in spite of the fact that at that temperature the pressure was still almost fifty pounds. We are unable to offer any explanation of this curious fact. The curve was continued to the axis of temperature in such a way as to resemble that of the other oil in the corresponding region.

Of chief interest is the relation of the four test-points to the corresponding explosion pressures.

1. In the low-grade oil, the Elliott flash-point coincides almost exactly with the beginning of the explosion curve. In the case of the high-grade oil, it cuts the curve at a point where the pressure is already greater than 25 lbs. This seems to indicate that the Elliott flash-point is of greatest

diagnostic value precisely in the case of those oils which are most dangerous to use.

For oil of any grade, the Elliott flash-point is the only one of the tests here employed, which in any sense heralds the approach of danger from explosion.

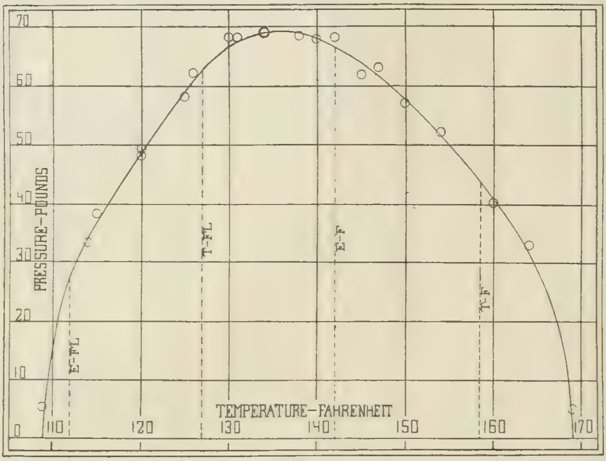


Fig. 4.—Sample No. 1.

2. For both grades of oil, the Tagliabue flash-point falls upon a point in the curve just short of the crest, where the pressure is already nearly as great as it is ever going to be. This test is therefore not an indication of the approach of danger from explosion, but rather of its arrival in full. Oil in a lamp is safer at almost any other temperature than that at which it flashes in the Tagliabue cup.

3. The fire-point in the Elliott cup gives about the same indication as the Tagliabue flash-point, except that the point of greatest danger is just passed, instead of being just at hand.

4. Finally, the Tagliabue fire-point lies in the region where explosions are hard to get at all, because the mixture is already too rich in vapor. In fact, in the case of the low-grade oil, it lies almost exactly at the point beyond which explosions become altogether impossible.

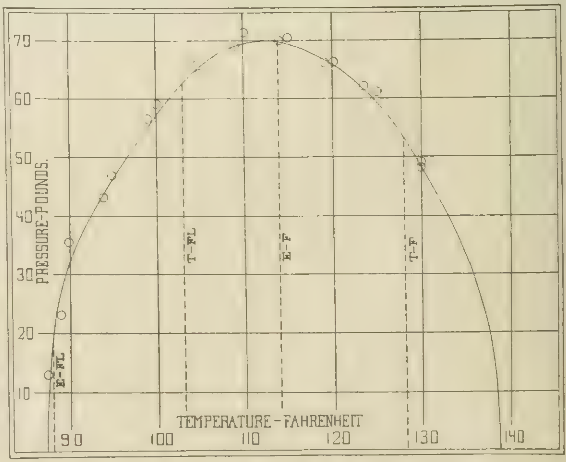


Fig. 5.—Sample No. 2.

While the results of these experiments do not afford direct information concerning the minimum flash-point consistent with safety, it is certain that that point should be higher than the temperature to which the oil in a lamp would be exposed. Observations with glass lamps equipped with a flat wick seem to indicate that the Elliott flash-point should not be lower than 100° F. But with the greater development of heat attendant upon the use of ring burners it would seem desirable to fix the point a few degrees higher than that. Kast and Rose,[1] using different styles of burners, including a "Rochester" circular burner, found that the temperature of the oil in the bowl of the lamp varied between 90° F. and 107° F. according to the burner employed, the room being at the ordinary temperature.

Again, it is not to be inferred from our results that the open cup tests are to be altogether disqualified. These tests, though indirect, are still of value if the standards are set with reference to the flash-point in the closed cup. Thus, if 100° F. is to be chosen as the minimum flash-point in the closed cup, then the limit for the open cup should be at least 115° F. Similarly, the fire-point in the closed cup should not be lower than 130° F., and in the open cup, 145° F. Each of these requirements,

[1] *Loc. cit*

though numerically so different, would furnish the same oil.

There are two possible sources of error in the method of measuring pressures employed in the foregoing experiments. One of these arises from the "dead space" below the piston of the indicator, which is not filled with the explosion mixture. The other is the small change in volume which is occasioned at the moment of explosion by the upward movement of the piston. Both of these render the observed pressure smaller than it otherwise would be. But it is obvious that neither of them could affect the general relation of the test-points to the pressure curve.

The only other variable factor in the experimental method lies in the possible influence which the size of the ignition spark might have. To test this, currents of different magnitudes varying from 0.5 to 2.0 amperes were used in separate experiments. Between these limits the explosions were regular, and the pressures obtained were concordant with one another. But when a current of less than 0.5 ampere was employed, the spark was so weak that occasionally no ignition followed at all, although when explosion was obtained it was concordant with those induced by the larger spark.

SUMMARY.

1. The explosion pressures of saturated mixtures of air and kerosene vapor have been measured over a range of temperature from a few degrees below the closed cup flash-point to several degrees above the open cup fire-point.

2. At the temperature of the closed cup flash-point the oil is already evaporating freely enough to produce a mixture which will yield an explosion pressure of several pounds, varying from about fifteen pounds in the case of a low-grade oil, to about twenty-five pounds for a high-grade oil. This test is the one which indicates most precisely the temperature at which danger from explosion begins.

3. At the temperature of the open cup flash-point the rate of evaporation is such that the mixture gives an explosion pressure almost equal to the maximum which can be obtained from the given sample.

4. At both fire-points the vaporization is so rapid that the mixture is too rich, and in consequence the explosion pressure is less than the maximum. At both temperatures the greatest danger from explosion is passed; at the open cup fire-point, indeed, long passed.

5. The maximum pressure was practically the same for high- and for low-grade oil, amounting to about seventy pounds gauge pressure.

Wesleyan University,
Middletown, Conn.,
Mar. 17, 1909.

ANALYSES AND FRICTION TESTS OF LUBRICATING GREASES.

By Horace W. Gillett.

Received March 19, 1909.

Since the first lubrication engineer applied a piece of fat meat to the squeaking axle of his primitive cart, practically everything that is greasy or slippery has been used in making grease. The term "lubricating grease" is one of the most comprehensive in the dictionary. In recipes given in works on lubrication we find as ingredients of greases, practically all known fats and oils, as tallow, palm oil, neatsfoot, rape, olive, sperm, castor, lard, corn, cottonseed, fish, all grades of mineral oil; soaps of sodium, potassium, calcium, magnesium, lead, zinc, aluminium and iron; rosin, rosin oil, bone tallow, wool grease, anthracene oil, paraffin, vaseline, ceresin, beeswax, Japan wax, bayberry wax, spermaceti, pitch, asphalt, naphthalene, rubber, glue, graphite, talc, infusorial earth, gypsum, magnesia, asbestos, mica, sulphur, Irish moss, kaolin, starch, wheat flour, sawdust, wood pulp, ground cork, ground glass, mercury, antimony, oxide of tin, lampblack, ivory, dust, water, acohol, glycerine, turpentine, carbonate of iron, lead sulphide, hair, borax and salt.

Though greases are of such varied composition, the literature of lubrication shows no comparison of the lubricating power of greases of different composition.

"Grease is grease" seems to be the attitude of most makers and users of that lubricant. The following work was undertaken in an attempt to determine the relation, if any, between composition and lubricating value of the typical greases on the market to-day.

Commercial greases may be divided into the following classes:

A. The tallow type: these greases are made up of tallow and more or less of an alkali soap, commonly the sodium or potassium soaps of palm oil, mixed with a smaller amount of mineral oil. These were the principal types of lubricating grease

ten or twenty years ago, but to-day are less used than the greases of type *B*.

B. The soap-thickened mineral oil type: these are the most common journal greases to-day, and are composed of mineral oil of various grades made solid by the addition of calcium or sodium soaps. Calcium soap is more used than sodium.

C. Types *A* or *B* with the addition of a mineral lubricant—usually graphite, mica, or talc.

D. The rosin-oil type: These consist of rosin oil thickened by lime, or less commonly, litharge, to which is added more or less mineral oil, either paraffin or asphalt oils being used. These are sticky, usually contain 20–30 per cent. of water, and find their chief application as gear greases where true lubrication is not so essential as prevention of wearing and rattling of the gears. Some very heavy bearings are occasionally lubricated with this type of grease. Tar, pitch, graphite and such fillers as wood pulp and ground cork are often put into these gear greases.

E. Non-fluid oils: these are thin greases stiffened to some extent with aluminium oleate or a mixture of soaps, as sodium and calcium.

F. Special greases, such as a mixture of wood pulp and graphite, thin greases of any of the above types mixed with wool or cotton fibers, hot-neck greases, freak greases containing rubber, etc.

Of these *A*, *B*, and *C* are the most important as lubricants.

The analysis of a lubricating grease may have one of two objects in view: to duplicate the grease, or to determine its value as a lubricant. Without resorting to mechanical tests of the actual friction reducing power of the grease in question, the first is probably the easier problem.

In the analysis of a grease, we may cover the following points:

Consistency.

Melting point.

Flash point.

Content of free acid.

Amount and nature of soap.

Ash, not alkali, from soap, nature and amount.

Mineral filler, as graphite, talc, etc., nature and amount.

Content of unsaponified, but saponifiable animal or vegetable fats or oils, nature and amount.

Content of unsaponifiable mineral or hydrocarbon oil, nature and amount.

Content of water.

The methods used in the analysis of the greases hereinafter described, was as follows:

Note first the odor and color. These may give clues of the probable composition, and will show if the grease is perfumed with nitrobenzol or any similar substance. Note the behavior on melting. The grease should melt to a clear homogeneous fluid. The oil should not melt away from the soap, since in such a case after being in the feed cup some time, the grease may change in composition, the oil running off the bearing and the soap staying behind.

The melting point is the most important single determination, as will be seen in the discussion of the friction tests.

This has been determined in various ways by various workers. One method is to use a closed capillary tube, after the usual way of taking melting points. Here it is very difficult to tell the exact point where the grease does become transparent and fluid. Moreover, the grease has to be melted into the tube, in which case it has to be laid away for several hours in order that it may regain its normal melting point.[1]

Another is the drop point, suggested by Pohl, in which the grease is smeared upon the bulb of a thermometer, or the thermometer dipped into the melted grease. The thermometer is then heated in an air bath and the drop point taken either as the point where the grease begins to flow and get thinner, so that the mercury of the thermometer bulb is seen, or when the drop actually falls off, according to the directions of different writers. This method is very inaccurate, owing to the large variation caused by the difficulty of getting the same amount of grease on the bulb each time, and through differences in the size and shape of thermometer bulbs.

Ubbelohde[2] gives a modification of this method that overcomes most of the difficulties, but for greases melting below 100° C., we have found the most satisfactory method to be the use of an open tube of 0.4 cm. internal diameter, and about 8 cm. long. This is stuck into the grease so that a plug of grease 1 cm. long is left in the glass tube. The tube is then attached by a rubber band to a thermometer so that the plug is beside the bulb. The thermometer with the tube attached is then immersed into a beaker of water so that the bot-

[1] Archbutt and Deeley, "Lubrication and Lubricants," 2d. Ed., p. 202.

[2] Holde, "Untersuchung der Mineralöle und Fette." Berlin, 1905, p. 209.

tom of the plug is 5 cm. below the surface. The water is then heated at the rate of 3°–4° C. per minute. When the melting point is reached, the plug, which is under a pressure of 5 cm. of water, slides upward in the tube. Checks can be obtained to 0.5° C.

The following tables show the effect of varying the different conditions:

Table I.—Effect of Diameter of Tube.

Plug 1 cm. long. Immersion 5 cm. Heating 3° 4° C per min.

Internal diameter.	Melting point
0.55 cm.	83.5° C.
0.50	83.5
0.40	84.0
0.30	84.5
0.15	85.5
0.10	86.0

Table II.—Effect of Length of Plug

Tube 0.4 cm. diam Immersion 5 cm Heating 3° 4° C per min.

Length of plug.	Melting point.
0.5 cm.	83.5° C
1.0	84.0
2.0	85.0

Table III.—Effect of Depth of Immersion

Tube 0.4 cm diam Plug 1 cm long. Heating 3° 4° C per min

Depth immersed.	Melting point
7 cm.	83.0° C
5	84.0
2	85.0

Table IV.—Effect of Rate of Heating

Tube 0.4 cm diam Plug 1 cm long Immersion 5 cm

Rate of heating. Per min	Melting point
1° C.	83.5° C
3° 4°	84.0
8°	84.5

The consistency at 20° C. was determined by a Legler consistometer which consists of a pointed glass rod, bearing a pan for weights, and supported by a spiral spring.[1] The grease was held at 20° C. for about an hour, and the total weight determined which was required to sink the rod into the grease exactly 1 cm. The spring was of such strength that it took 20 grams to depress the rod 1 cm. in air, and this 20 grams was subtracted from the total weight required, to give the consistency number. This varied in different commercial greases from 200 grams to 4 grams. Readings could be checked to within 5 per cent. of their value. The instrument gave a consistency number for the pasty mass consisting of 50 per cent. stearic and 50 per cent. oleic acids, of 75–80 grams. All the weights must be on the pan before it is released, as the penetration is less if the weights are added while the rod is falling. Attempts to take the time required for the rod to sink a certain

[1] *Chem. Ztg.*, **1884,** VIII, 1657; *Chem. Ctrbl.*, **1884,** XV, 734. Benedict and Lewkowitsch, "Oils, Fats and Waxes," **1895** Ed., p. 74.

distance were unsuccessful, as the greases varied so much in consistency that the same weight could not be used for all, which would be essential for comparative results by the timing method. Hence recourse was had to the weight required to sink the rod a given distance. The measurement of the consistency is a well recognized part of the examination of a lubricating grease,[1] yet, as shown in Table X, it has no direct bearing on the lubricating power. Its value lies chiefly in showing what sort of a grease cup should be used for that particular grease, whether gravity, compression, etc.

The flash-point is taken in a 50 cc. porcelain crucible filled with the grease, into which is stuck the bulb of a thermometer. The crucible is heated at 5° C. per minute on a sand bath, and the flash determined by noting the temperature at which a 3 mm. gas flame passed over the crucible at 2° intervals causes a flash to pass over the surface. The chief value of this determination is to give some idea of the grade of mineral oil used in compounding the grease.

The content of free acid is obtained by dissolving or disintegrating, if not completely soluble, 2.82 grams of the grease in a neutral mixture of alcohol and ether containing phenolphthalein. The grease is then titrated with N/10 KOH to pinkness, each cc. of alkali used equaling 1 per cent. of free acid, figured as oleic. Most commercial greases run almost neutral, 0.5 per cent. being high, though as high as 6 per cent. has been found. Greases that contain unsaponified palm oil are especially likely to show free acid. The importance of neutrality is very great, because of the corrosion of the bearings by free acid.

The determination of the soap content may be made in several ways. The bases may be thrown down as oxalates from a turpentine-benzine-alcohol solution by oxalic acid, after the method of Conradson[2] and the soap content figured from the amount of base found. The soaps may be determined by Holde's method of decomposing the soaps by mineral acid, washing out the mineral acid, and titrating the fatty acids thus freed, and from the titration figuring the amount of soap.

The simplest and shortest method, however, in practically every case, is to ash the grease,

[1] Benedict and Lewkowitsch, *Loc. cit.* Archbutt and Deeley, "Lubrication and Lubricants," 2d Ed., p. 162.

[2] *Jour. Amer. Chem. Soc.*, XXVI, **6,** 705.

titrate the Na_2CO_3, K_2CO_3 or CaO in the ash with acid, and figure the soap content from the titration, one cc. of N/2 acid being equivalent to

0.1612 gram potassium stearate,

0.1535 gram sodium stearate,

0.1520 gram calcium stearate.

If the Liebermann-Storch rosin test shows the soap to be partly a rosin soap and rosin oil is absent, this will give low figures, owing to the higher combining weight of abietic than that of stearic or oleic acids. In such a case, if extreme accuracy is required, the fatty acids of the soaps may be freed, and rosin determined by Twitchell's method. Ordinarily, this would not be required.

In the case of greases made with sodium or potassium soaps, the soap may be directly determined after extraction in a Soxhlet of the unsaponified and unsaponifiable fats with ether, by extraction of the residue from the ether extraction, with alcohol. With lime soaps this method fails, owing to the large solubility of calcium soap in all solvents for fats, as well as its insolubility in alcohol. It would greatly simplify the analysis of greases containing calcium soap if some solvent could be found that would extract fats and oils without extracting any of the lime soap, in the same way that ether may be used to separate the fats and oils from the soap in a soda soap grease. In attempting to make an ether extraction of a lime soap grease, we have repeatedly found from 1/4 to 1/3 the total lime in the ether extract, owing to the solubility of the calcium soap.

Gasoline extracts nearly as much. Numerous experiments have been made with other solvents and mixtures of solvents, but no satisfactory one has been found. Ethyl acetate at room temperature dissolves but little of the calcium soap, and the extract will give a fair qualitative idea of the nature of the oil used in compounding the grease.

If the grease is made up with a lead soap, the lead may be determined by decomposing the grease by boiling with a mixture of sulphuric and nitric acids, after the Neumann acid ashing method, and weighing the lead sulphate.

The nature of the base used in the soap may be determined by the usual methods, or more quickly and delicately, by microchemical methods. A small amount is ignited on a porcelain crucible cover, the ash dissolved in dilute HCl and three drops of the solution put on a microscope slide. To the first drop is added a small drop of dilute H_2SO_4, and to the second a small drop of H_2PtCl_6. The third is evaporated to dryness over a microburner, and a drop of a concentrated solution of uranium acetate slightly acidified with acetic acid, is added. The three drops are then examined under the microscope. The first will show the characteristic sheaf-like groups of gypsum crystals if lime is present, or the fine white granular plates and rhombs of $PbSO_4$ if lead is the base used. The second will show the yellow octahedra of K_2PtCl_6 if potassium is present, while the third drop will show the tetrahedra of the double acetate of uranium and sodium, if we are dealing with a soda soap.[1]

The amount of ash other than alkalies from the soap may be determined by the difference between the total ash and the alkali found by titration. Greases contain from zero to sometimes one per cent. of adventitious dirt, iron and aluminium oxides, silica, etc.

In the case of a grease of type C, containing graphite, talc, etc., the mineral filler may be determined directly after extraction with ether and then with alcohol, if we are dealing with an alkali soap, or in any case, by weighing the ash insoluble in acid. In the case of graphite, care should be taken to ash at a low temperature to minimize the oxidation of the graphite.

The unsaponified saponifiable matter, in the case of a grease made with an alkali soap, is best determined by saponification of the ether extract with alcoholic potash. The nature of the saponifiable may be found by evaporating off the alcohol after saponification, extraction of the unsaponifiable with ether, freeing the fatty acids from the soap left behind, and taking the melting point, iodine number and refractive index of the fatty acids, and thus identifying the fat from which the acids come. This is simple if only a single fat was used, but less so in a mixture. In most cases where a grease contains unsaponified saponifiable matter, it has been made by a partial saponification of the fat in question, and so the original grease may be saponified directly, and the total fatty acids examined.

In a calcium soap grease, the soap may be decomposed by heating with dilute HCl, washing, saponifying the freed fatty acids with alcoholic soda, evaporating the alcohol and extracting the

[1] For a full description of these extremely delicate and rapid microchemical methods, which are so valuable but so little known, see Behrens, *Microchemische Analyse*, or a series of articles by Chamot in *Jour. App. Microscopy*, Vols. III, IV

mixture of soda soap and unsaponifiable, which is now in the condition of a grease originally made with soda soap, with ether. This gives us the unsaponifiable, and we may proceed with the examination of the fatty acids in the soap as above. The unsaponifiable ether extract will consist of mineral or hydrocarbon oil, and the specific gravity, flash pont and refractive index will show us the nature of the mineral stock. In a rosin oil grease we may treat the mixture of rosin oil and mineral oil by any of the usual methods for quantitative separation or estimation, none of which, however, are very satisfactory.

The determination of water in lubricating greases is usually made either by the delightfully simple method of "determination by difference" or by drying down to constant weight. Archbutt and Deeley[1] advocate drying at 105°–110° C. until frothing ceases. Wright[2] drys at 105° till the weight is approximately constant at half-hour intervals of weighing. Hurst[3] drys at 220° F. to constant weight. Conradson[4] takes moisture by difference, but recognizes the fact that some oil is volatilized at 100° C. Holde[5] says: "The old method of mixing a weighed portion with alcohol, heating till no more bubbles appear, cooling and weighing, only gives useful results in the absence of light, volatile oils. More general is the application of the Marcusson xylol method.[6] By this method, six greases gave from 1 to 6.3 per cent. water, the difference between checks on the same grease being 0 to 0.2 per cent. By other methods the water content came from 0.5 to 2.2 per cent. too high."

Our attention was first drawn to this by a series of greases rather high in water content which were dried in the water oven to an apparent constancy of weight, but lacked several per cent. of adding up to 100. On investigation it was decided that the water determination was the weak point, and determinations were made by the xylol method, when the analyses added up well. Further work showed that though in this case the moisture determinations by drying were too low, in general drying to constant weight gives high results, as claimed by Holde.

Table V shows the results obtained by drying down a lead-rosin oil grease (No. 9, Table X). Ten grams were dried in wide-mouthed drying bottles provided with a glass rod for stirring the grease. Two xylol distillations were made on 10 grams each, giving 2.48 and 2.46 cc. water, an average of 24.7 per cent. moisture.

TABLE V.—LEAD ROSIN OIL GREASE.

(A) Hours at 110° C.	Per cent. loss.	(B) Hours at 95°–100° C.		Per cent. loss.
2	16.49	2		11.50
6	22.66	6		14.98
11	25.35	11		18.22
13	25.11	13		18.94
15	27.67	15		19.47
17	28.27	17		19.98
19	29.06	19		20.26
21	29.61	Hours at 105°–110°	Total	
25	29.90	2	21	23.79
30	30.53	4	23	25.63
..	...	8	27	26.36
..	...	12	33	28.54

TABLE VI.—SODA GREASE (NO. 12, TABLE X).

This contained no water by anhydrous $CuSO_4$ or by xylol distillation.

Hours at 105°–110° C.	Per cent. loss.
1	0.26
7	1.13
8	1.23
12	1.69
18	2.12
23	2.44

TABLE VII.—(SEE FIG. 1) WINTER MOTOR GREASE (NO. 3, TABLE X).

Moisture by xylol 0.03 per cent. Anhydrous $CuSO_4$ shows only faintest trace moisture.

A. Hours at 105° C.	Per cent. loss.	B Hours at 95°–100° C	Per cent. loss.
2	2.3	2	1.3
5	2.9	5	1.6
7½	3.4	7½	1.8
11	3.8	11	2.1
13	3.9	13	2.25
16	4.1	16	2.4
20	4.4	20	2.6
23	4.6	23	2.8
28	5.0	28	3.1
31	5.1	31	3.25
34	5.25	34	3.35
38	5.35	38	3.45
40	5.50	40	3.55
43	5.82	43	3.67
46	5.90	46	3.75
50	6.04	50	3.85
52	6.34	52	3.96
54	6.47	54	4.06
61	6.71	61	4.36
*64	7.38	*64	4.75
67	7.43	*67	4.90
70	7.70	*70	5.10

*61 to 64 on A at 120°.

*54 to 61 on B at 105°
*61 to 64 on B at 120°
*64 to 70 on B at 105°

Another calcium soap grease showing a faint trace of moisture by anhydrous $CuSO_4$ and 0.05

[1] "Lubrication and Lubricants," p. 306.

[2] "Analysis of Oils and Allied Substances," p. 104.

[3] "Lubricating Oils, Fats and Greases," p. 281.

[4] *Jour. Amer. Chem. Soc.*, XXVI, **6**, 705, June, 1904.

[5] "Untersuchung der Mineralöle und Fette," 2d Ed., p. 213.

[6] J. Marcusson, 1904. "Bestimmung des Wasser und Saüres-Gehalten von Schmierfetten," *Mitt. K. Materialsprufungsamt*, **24**, 48; "von Die Bestimmung des Wassergehaltes von Ölen, Fetten, Seifern, Harzen usw.," *Mitt. K. Mater.*, **23**, 58. See also Hoffmann, *Z. angew. Chem.*, **21**, 2095; *Chem. Abstr.*, **3**, 2, 158 (Jan. 20, 1909).

per cent. by xylol, gave a loss of 2.30 per cent. on heating 30 hours at 105°-110°.

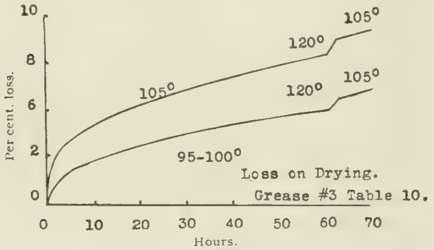


Fig. 1.

TABLE VIII.—TALLOW GREASE (NO. 7, TABLE X).

This showed moisture by $CuSO_4$ and gave 2.48% and 2.51% by xylol distillation.

Hours heated.	A at 110°. Per cent. loss.	B at 95°–100°. Per cent. loss.
2	3.70	1.71
5	4.78	2.55
7	5.11	3.09
11	5.21	2.55
14	5.30	4.50
17	5.36	4.81
19	5.39	4.96
23	5.50	5.16
25		5.24

Another sample of this lost 2.66 per cent. in 2 hours at 110° C., half a cc. of water having been added to the grease, and the 2.66 per cent. being corrected for this added water. This, after heating for two hours, gave no test for water by $CuSO_4$, but further heating of this at 110° till it approached constant weight showed a loss of 5.3 per cent. in 23 hours, showing that volatile matter was being driven off.

TABLE IX.—A COMMERCIAL TALLOW SHOWING NO TURBIDITY ON MELTING AND NO TRACE OF MOISTURE BY $CuSO_4$ OR XYLOL. HEATED AT 105°–110°. SHOWED

Hours heated.	Per cent. loss.
2	0.59
4	0.84
6	0.85
9	1.02
12	1.10
14	1.12
17	1.13

One drop of water stirred into 15 grams of this tallow showed moisture by $CuSO_4$ and by distillation with xylol.

The curve in Fig. 1 shows that as the temperature was raised, the loss increased, as is seen from the pitch of the curves.

These tables show that in practically all types of commercial greases, drying down to constant weight gives high results. The results obtained by the xylol distillation in every case agreed with what we would expect from $CuSO_4$ and other moisture tests. Moreover, there are no sharp breaks in the curves, by which we can tell just when the water has been driven off. In drying down ether extracts from greases, some loss is therefore also to be expected, but it is better to add this loss to the oil, than to ascribe it to moisture.

To determine the moisture in a lubricating grease, then, we first test it with anhydrous $CuSO_4$ if the grease is sufficiently light in color. If water is present, or in the case of a dark grease, we weigh out 10 gr. on a balanced filter paper, put the grease and paper in a 300 cc. Erlenmeyer flask and cover with xylol. The xylol should be distilled from water and separated out from the water after clearing, in a separatory funnel. The flask, connected with a dry condenser, is heated in a bath of cylinder oil, and the xylol and water slowly distilled off till the xylol comes over clear. The bulk of the water comes over with the first 10 cc. of distillate. The distillate may be caught in a burette filled with water up to the lowest graduation, best with a few drops of xylol added to give the same meniscus as we will read, or in a receiver made like a funnel, with a graduated stem closed at the bottom, according to the method of Dean,[1] and allowed to stand over night, or till all milkiness has disappeared. A still better and more rapid method we find to be to catch the distillate in centrifuge tubes such as are used in urine analysis. The fine graduations allow of very accurate reading. Bulbs holding about 50 cc. are blown on the tops of these tubes, and the modified tubes containing the xylol-water mixture whirled in a larger centrifuge than the one they were designed for. This obviates the necessity of waiting for the xylol to clear up. A complete moisture determination may be made in 45 minutes.

Absolute accuracy in the determination of water in the technical examination of lubricating greases, is doubtless not important, though Holde has recently shown[2] the great influence exerted by even 1 per cent. of water on the drop point and the emulsified condition of lime soap greases. Every one who has driven off the water from a lime soap grease containing even a few hundredths of a per cent. of water, has noticed the change from a buttery opaque mass to a gelatinous trans-

[1] A. L. Dean, "The Estimation of Moisture in Creosoted Wood," Forest Service Circular 134, Jan., 1908.

[2] Holde, "The Physical Condition of Solid Fats, and of Solutions of Calcium Soaps in Oil," *Petroleum*, IV, 1, 14, Oct. 7, 1908, *Z. angew. Chem.*, **31**, 2138-44 (1908); *Chem. Abstr.*, **3**, 1, 123 (1909).

lucent one. Although not particularly important in the case of greases the fact that the xylol method gives more accurate results than that of drying down, is of importance in the analysis of other commercial products containing water.

Thirteen commercial greases were analyzed according to the methods given above, with the following results:

TABLE X.

No	Name.	Flash-point. Degrees C.	Consistency. Grams, 20 C.	Melting point. Degrees C.	Per cent. calcium soap.	Per cent. other thickeners.
1	Graphite	195	18	93	11	16% Graphite
2	Summer motor.	160	170	87	38	..
3	Winter motor..	175	7	86	23	..
4	K 1	193	24	85	16	..
5	K 2	195	66	93	20	..
6	Auto	190	11	79	19	..
[1]7	Tallow A......	210	150 (estimated)	52	..	1.4 Potash soap.
[1]8	Tallow XX.....	215	200	49	..	2 1% Potash soap. 30% Paraffin
9	Lead rosin oil...	240	7	102	..	1.75% Lead
10	Lime rosin oil...	198	31	77	..	9.9% CaO
11	Lime rosin oil...	198	4	75	..	7.8% CaO
12	Soda grease......	215	35	83	..	22% Sodium soap.
13	Non-fluid oil...	210	27	76	9.8	12.9% Sodium soap.
14	No. 4 Petrolatum.........	247	6	47	..	..
15	Lard oil.......	265	0	5	..	..

TABLE X—(*Continued*).

No.	Name.	Per cent. H_2O.	Per cent. saponifiable oil	Per cent. free acid as oleic.	Per cent mineral oil.
1	Graphite................	trace	17	0	56
2	Summer Motor..........	0.05	25	trace	36.5
3	Winter Motor...........	0.03	37[2]	6.1	40
4	K 1.....................	0.2	16	0	67
5	K 2.....................	0.3	20	0.3	60
6	Auto....................	1.0	20	trace	60
7	Tallow A...............	2.5	73.5	0	22
8	Tallow XX......	trace	48	0	20
9	Lead Rosin.............	24.7	0	0	....
10	Lime Rosin.............	trace	0	0	....
11	Lime Rosin.............	20.0	0	0	. . .
12	Soda Grease............	0.0	0	0	78[3]
13	Non-fluid Oil............	0	7	0	70.3
14	No. 4 Petrolatum.......	0	0	0	100
15	Lard Oil	0	100	....	0

TABLE X—(*Continued*).

No.	Name.	Maximum temp. of bearing above room temp. Deg. C.	Coefficient of friction at end of 3-hour run.	Coefficient of friction. Average throughout 3-hour run.
1	Graphite	53	0.108	0.097
2	Summer motor.	39	0.075	0.075
3	Winter motor..	42	0.063	0.063
4	K 1..........	38	0.054	0.057
5	K 2..........	39	0.050	0.054
6	Auto..........	32	0.046	0.046
7	Tallow A .	22	0.012	0.022
8	Tallow XX	25	0.018	0.029
9	Lead rosin .	40	0.050	0.067
10	Lime rosin	42	0.017	0.048
11	Lime rosin .	29	0.025	0.036
12	Soda grease ..	17	0.016	0.019
13	Non-fluid oil....	25	0.016	0.026
14	No 4 petrolatum	16	0.018	0.018
15	Lard oil.......	7	0.010	0.011

[1] Scented with nitrobenzol.
[2] Chiefly palm oil.
[3] Oil of 24.2° Bé.

Friction tests were then made on these and on a petrolatum (Standard Oil No. 4), and on a pure lard oil, as standards of reference.

The testing machine was a small Thurston, fitted with a compression grease cup, through which the grease was allowed to feed freely. The temperature was taken by a thermometer sunk in a small well filled with oil in the upper brass. The Fahrenheit thermometer supplied with the instrument was not sufficiently delicate, and was replaced by a small Centigrade one. The temperature of the bearing and the arc at which the pendulum stood, from which the coefficient of friction is figured, were noted at intervals of one minute for the first hour, and at every five or ten minutes thereafter. The temperature of the room was taken periodically, and the r. p. m. noted.

The total pressure on the bearing in all cases was 240 lbs., equivalent to 60 lbs. per square inch projected area of the bearing. This was the highest pressure that could be obtained with the machine. It is probable that at higher pressures the differences between the greases would be still more marked.

The speed was kept constant at 310–320 r. p. m. by a shunt-wound motor.

The general behavior of a grease during the run was as follows: at first the coefficient of friction would be high, and the temperature would rise rapidly. In the case of a hard grease, as a rule, this would continue until the thermometer showed some certain temperature, nearly up to the melting point of the grease. The surface of the bearing probably did reach that temperature, although the thermometer did not register quite that temperature, as there was some chance for radiation.

After the grease had apparently melted, and the bearing was then in the state of an oil-lubricated bearing, the coefficient of friction would momentarily fall off, sometimes to a very low figure, and the temperature would drop rapidly. Then the grease would seem to stiffen again, and the coefficient and temperature would immediately rise again. The graphite grease (Fig. 2) shows this behavior to the greatest extent. This would

go on for perhaps an hour, when a condition of equilibrium would be established, and a fairly constant reading would be attained. Many of these momentary fluctuations are smoothed out of the curves as here plotted, by taking averages of five- or ten-minute periods and plotting those. Figs. 2 to 9 show the curves for seven typical greases. The temperature plotted in the curves is the actual temperature registered by the thermometer; that given in column 12, Table X is the temperature of the bearing above that of the room.

Since the friction cannot be reduced till the temperature of the bearing has risen enough for the grease to melt, or at least to be softened so it can flow over the bearing, it follows that other things being equal, the grease with the highest melting

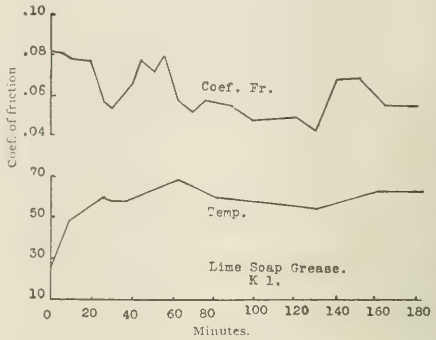


Fig. 4.

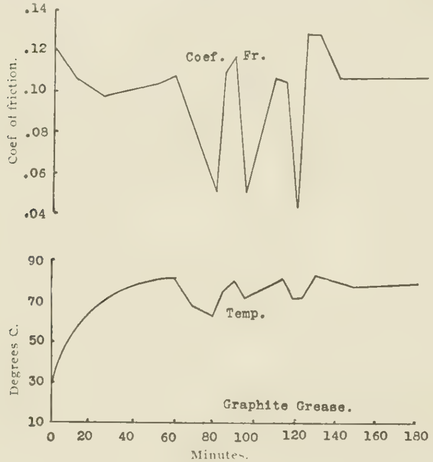


Fig. 2.

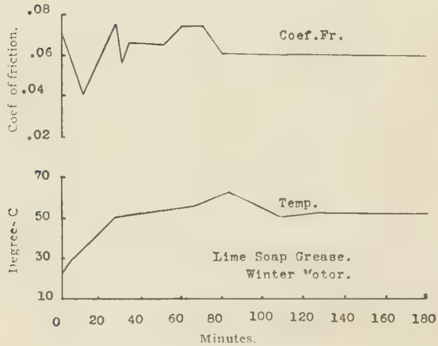


Fig 3

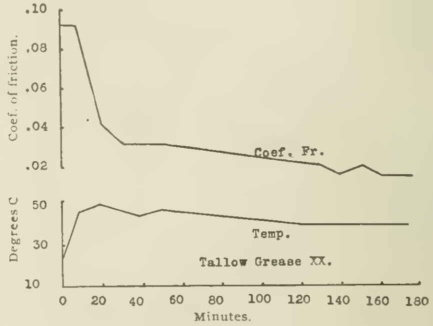


Fig. 5

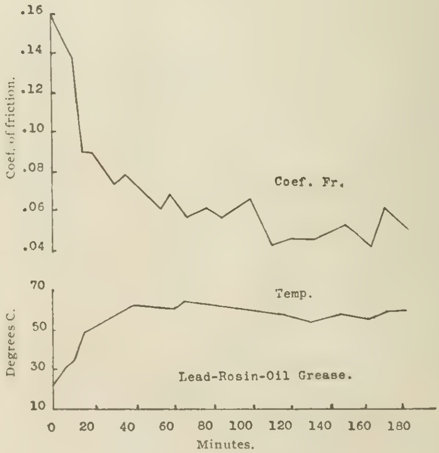


Fig 6.

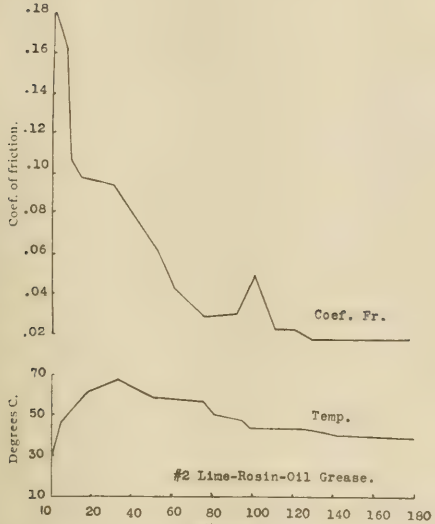


Fig. 7.

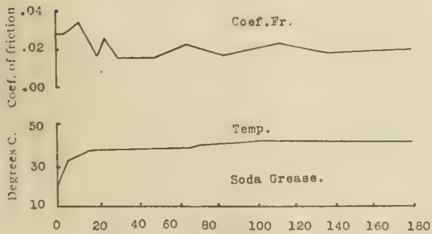


Fig. 8.

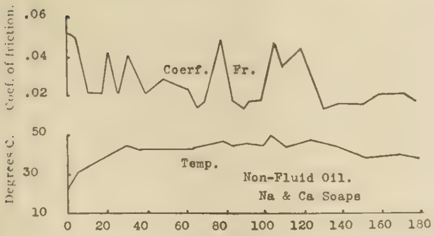


Fig. 9.

point will produce the highest coefficient of friction. Hence the lowest melting grease that will stay on the bearing will have the lowest coefficient of friction, which is only another way of saying that a grease already melted, *i. e.* an oil, will give the best results wherever it can possibly be used.

The average coefficient of friction tabulated in column 14 of Table X is found by plotting the coefficients for each reading against the time in minutes, and taking the average from the curve. Duplicate runs on the same grease gave very good checks, the fluctuations did not, of course, come at exactly the same minute of the different runs, but the general trend of the curves was the same, and the average coefficient of friction for a three-hour run would check within about 5 per cent.

There is no direct proportionality between the results of the determination of any one analytical constant, and the lubricating power though there seems to be an approximate relation between the melting point and the friction reducing power, as would be expected. This is shown in Fig. 10.

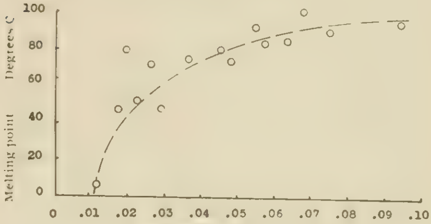


Fig. 10.

The relation, however, is not close enough to allow us to predict the lubricating value from the melting point without taking the chemical composition and the physical constants into consideration.

The graphite grease showed an unexpectedly low lubricating power, and would be best fitted for a gear grease. The rosin oil greases, which are usually considered to be very poor lubricants, showed high friction at first, but after the bearing had warmed up enough to soften them somewhat, they compared well with the more expensive greases. The high moisture content of most of these greases would seem to be no drawback, but rather an advantage in rendering them less sticky.

It will be noted that the lime soap greases, the most common type to-day, do not give as good results as the older, though more expensive type of tallow greases. It will also be seen that the greases compounded with soda soaps are better lubricants than those compounded with lime soaps.

This work was begun at the suggestion of Mr. A. D. Little, of Boston, and was carried on almost entirely in the Arthur D. Little Laboratory

of Engineering Chemistry while the writer was a member of the laboratory staff.

Sincere thanks are due Mr. R. P. Tobin, of Boston, for the loan of the Thurston testing machine.

CORNELL UNIVERSITY.

[CONTRIBUTION FROM THE NEW YORK TESTING LABORATORY.]

COMMERCIAL PYRIDINE AND ITS VALUE AS A SOLVENT.

BY KENNETH G. MACKENSIE.

Received April 3, 1909.

Bedson has shown[1] that pyridine may be used as a solvent to distinguish and separate the constituents of coal. His work suggested a similar use in the examination and analysis of the various bitumens and rubber. To this end, on the recommendation of Prof. Bedson, this laboratory imported a quantity of pyridine from Brotherton & Company, Ltd., Sunderland, England. A series of preliminary tests gave the following results:[2]

Parts soluble of	Pyridine. Per cent.	Carbon disulphide. Per cent.
Bermudez refined asphalt	23.0	98.6
Trinidad refined asphalt	22.0	56.0
"J" grade asphalt	27.0	99.0
Gulf residual pitch	20.0	97.5

Rubber was apparently insoluble in commercial pyridine.

These results led to suspicions of the purity of the pyridine, and a kilo was distilled, using an eighteen-column Young dephlegmator.

COMPOSITION OF SAMPLE OF PYRIDINE.

Distillate.	Temperature.	Per cent.
I	86.0– 94.4° C.	1.0
II	94.4	26.1
III	94.4–105	0.6
IV	105.0–112.0	0.8
V	112.0–115.0	1.4
VI	115.0–116.0	4.5
VII	116.0–116.7	3.2
VIII	116.7–117.2	12.5
IX	117.2–118.0	10.5
X	118.0–121.0	5.0
XI	121.0–123.0	1.3
XII	125.0–131.0	4.6
XIII	131.0–134.0	1.7
XIV	134.0–136.0	8.5
XV	136.0–140.0	4.6
XVI	140.0–144.5	1.0
XVII	144.5	5.2
	Residue	7.5
		100%

Distillate I.—Consists of two liquids of different gravity, which were miscible on agitation. The odor of benzene was plainly perceptible above the characteristic pyridine odor.

[1] *J. Soc. Chem. Ind.*, **27**, 147.
[2] By Mr. R. H. Parker.

Distillate II.—This substance had a most remarkable constancy of boiling point. In spite of repeated distillations the figure 94.4° was always obtained. It has the following constants:

Specific gravity	15° C./15° C.	1.008
Refractive index	25° C.	1.4418

Goldschmidt and Constam[1] isolated from coal-tar "a pyridine" fraction boiling at 92–93°, having a specific gravity of 1.0219. This was found to be a definite hydrate, $C_5H_5N.3H_2O$. On treatment with solid KOH and distilling, they obtained a distillate 114–116°, which analyzed for pyridine.

Distillate II was accordingly treated in a similar manner. Nothing whatever appeared on distilling from solid KOH, below 110°, almost all going over at 115–117°. That portion at 115–117°, gave, after drying the platinum salt at 100°:

	Found.	Calculated $(C_5H_5NHCl)_2PtCl_4$
Pt	34.18 %	34.34%

Distillate II was approximately synthesized as follows: 40 grams water were mixed with a sufficient excess of pure pyridine, and distilled. 66 grams came over at 94.4–95°, the temperature then jumping to above 110°. Theory requires 67 grams of $C_5H_5N.3H_2O$.

From these figures it is seen that Distillate II is identical with the hydrate of Goldschmidt and Constam; and that, furthermore, *instead of the indefinite boiling point 92–93°, assigned to it by them, it boils very constantly at 94.4°.*

Distillates VI to IX.—

Specific gravity	15° C./15° C.	0.983
Refractive index	25° C.	1.5051

The usually accepted boiling point of pyridine is 116.7°, though it is given as 114.5° by Kahlbaum,[2] as 116–116.2° by Schiff,[3] as 115.51° by Louguinine,[4] and as 115.2° by Constam and White.[5] Its specific gravity, according to Perkin,[6] at 51° is 0.9855, Constam and White give at 15°/4° 0.989305, and Trobridge[7] at 14°, 0.9893. Its refractive index by Nasini, Brühl[2] is 1.51290, and by Constam and White at 17° 1.51068, and by Trobridge at 14° 1.5124.

These distillates may be classed as pyridine.

Distillate X.—

Specific gravity	15° C./15° C.	0.9765
Refractive index	25° C.	1.5032

[1] *Ber.*, **16**, 2976.
[2] Siedetemp. u. Druck, 95.
[3] *Ber.*, **19**, 566.
[4] *Compt. rend.*, **128**, 367.
[5] *Am. Chem. J.*, **29**, 2.
[6] *J.Chem. Soc.*, **55**, 701.
[7] *J. Soc.Chem. Ind.*, **28**, 230.
[8] *Zeit. Ph. Ch.*, **16**, 214.

Distillate XI.—

Refractive index.......	25° C.	1.5020

Distillate XII.—

Specific gravity........	15° C./15° C.	0.955
Refractive index.......	25° C.	1.5009

Analysis of platinum salt, dried at 100° C:

	Found.	Calculated for picoline. $(C_6H_7NHCl)_2PtCl_4$
Pt...........	32.77%	32.72%

A picoline, first found in coal-tar by Goldschmidt and Constam, has a boiling point of 129°, according to Ladenburg and Lange.[1] Thorpe[2] gives 133.5° corrected. Weidel[3] reports that a picoline comes over 133–140°. Garrett Smythe[4] gives 129.5° (763 mm.) and Constam and White 128.8°.

Its specific gravity at 0°/4° is 0.9652 (Ladenburg and Lange); at 0°/4° 0.9616, and at 10° 0.95257 (Thorpe); at 15°/4° 0.94972 (Constam and White); and Trobridge at 14°, 0.9530.

Its refractive index by Gladstone[5] is 1.5006, by Constam and White 1.50237, and by Trobridge at 14° 1.4966.

From this it is concluded that Distillate XII must be a picoline.

Distillate XIV.—

Specific gravity.......	15°/C./15° C.	0.946
Refractive index......	25° C.	1.5022

Analysis of platinum salt, dried at 100° C.:

	Found.	Calculated picoline.	Calc. $(C_7H_9NHCl)_2PtCl_4$ lutidine.
Pt.................	32.55%	32.72%	31.26%

Distillate XVII.—

Specific gravity......	15° C./15° C.	0.947
Refractive index......	25° C.	1.5026

Analysis of platinum salt, dried at 100° C.:

	Found.	Calculated picoline.
Pt................	32.90%	32.72%

β-Picoline, was found in tar by Mohler.[6] It boils according to Schwarz and Stöhr[7] at 143.5°. Constam and White give 143.4°. Specific gravity by Schwarz and Stöhr at 0°/4° is 0.9726; by Constam and White at 15°/4° 0.96134. Its refractive index is given by Constam and White at 18° as 1.5720.

γ-Picoline was first found in tar by Schulze[8] and Ladenburg.[9] Beilstein gives its boiling point as 142.5–144.5°; Constam and White give 143.1°.

[1] A., **247**, 6.
[2] *J. Chem. Soc.*, **37**, 223.
[3] *Ber.*, **12**, 2008.
[4] *J. Chem. Soc.*, **81**, 452.
[5] *Ibid.*, **45**, 246.
[6] *Ber.*, **21**, 1007.
[7] *Ibid.*, **20**, 413.
[8] *J. pr.* (2). **43**, 154.
[9] *A.*, **247**, 10.

Its specific gravity (Beilstein) at 0°/4° is 0.9742; at 15°/4°, 0.95714 (Constam and White); at 12.5°, 0.9603 (Trobridge).

Its refractive index (Constam and White) is 1.50640 at 17°. Trobridge gives 1.5065 at 12.5°.

Distillate XVII must be either β- or γ-picoline, or a mixture of both. Its specific gravity and refractive index are nearer that of the γ-position. Trobridge, moreover, finds only the γ-isomer in his pyridine base faction 145–150°. This distillate must be γ-picoline.

Distillate XIV, though not corresponding exactly with any of the picolines, comes nearest to the α-position, and must of necessity be placed there.

THE SOLVENT ACTION OF PYRIDINE, ETC.

In making the solubility tests, three portions were used: (*a*) the hydrate boiling at 94.4°; (*b*) distillates VI–IX boiling at 115–118°, designated "pure pyridine;" and (*c*) distillates XIV–XVII boiling at 134–144.5°, designated "picolines."

	CS_2.	Hydrate.	Pyridine.	Picoline.
Bonanza Gilsonite.—				
Per cent. soluble.......	99.7	1.7	96.1	99.5
Bermudez Refined Asphalt.—				
Per cent. soluble......	95.3	2.8	94.8	95.6
Gulf Residual Pitch.—				
Per cent. soluble.......	96.8	2.1	96.8	97.4

Dry Sample of Rubber, having on a dry basis the following composition, as determined by the use of acetone as a solvent:

	Per cent.
Resins.....................	18.5
Rubber.....................	67.9
Insoluble..................	13.7

	Pyridine hydrate.	Pyridine.	Picolines.
Per cent. soluble..........	7.0	71.8	88.0

Wurtzelite.—

	CS_2.	Chloroform.	Picolines.
Wurtzelite, No. 72684—			
Per cent soluble ..	6.53	8.73	10.1

The above figures show that the inability of commercial pyridine to dissolve bitumens to any considerable extent is due to the presence of water, which forms with the pyridine a hydrate with very little solvent action. Likewise, the further up we go in the pyridine series, the better solvents we obtain.

Summary.—Commercial pyridine consists of pyridine, picolines and water. The water forms with pyridine a definite hydrate which boils exactly at 94.4°. This hydrate has very little solvent action on bitumens, and by its presence in pyridine materially decreases the solvent action

of that base. The picolines are even better solvents than pyridine, in some cases being equal to and even surpassing carbon disulphide.

FLASH AND FIRE OF PYRIDINE DERIVATIVES

	Flash.	Fire.
Hydrate, 40 per cent water ..	35° C	55° C
Pyridine....................	17°	17°
Picoline 125–131............	25°	30°
" 134–136..............	33°	40°
" 1445.............	42°	48°
Crude pyridine..............	31°	38°

Apparatus = 4 oz. open tin dish 2–1/4" diameter.

NEW YORK TESTING LABORATORY.
MARCH 31, 1909.

PURITY OF COMMERCIAL LIQUEFIED AMMONIA GAS AND APPARATI FOR TESTING IT.[1]

By DR. F. W. FRERICHS.

The following paper discusses the purity of commercial liquefied ammonia and describes the principal apparati, which have been proposed for testing its purity in the United States and in Europe.

The test is based upon the low boiling point of liquefied ammonia gas, which is 28° F. below zero, and upon the consideration that the impurities, which are likely to be present, have a much higher boiling point. Therefore if a sample of liquid ammonia be evaporated the impurities contained in same would probably remain in the vessel, and their quantity could be ascertained. Liquefied ammonia gas now is considered good by American ice manufacturers if no visible residue is left in a flask in which a 4 oz. sample has been evaporated.

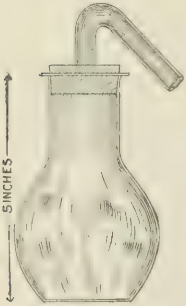


Fig. 1.

Fig. 1 shows a test bottle similar to the one in common use in the United States, and Fig. 2 shows the mode of drawing a sample from a cylinder of ammonia.

This mode of testing gives only approximate results. One source of error is the moisture contained in the surrounding atmosphere. On account of the rapid evaporation of the liquid ammonia, the iron tube by which the sample is drawn becomes very cold and so does the flask, and moisture from the air will readily condense upon the cold surfaces. By drawing the sample quickly, and closing the flask at once with a perforated cork carrying a bent glass tube, contamination of the sample with moisture is as much as possible, but never entirely, prevented. But the fundamental source of error in this method of testing rests in the fact that small quantities of the impurities often contained in the commercial ammonia will evaporate with the ammonia used for the sample, on account of which fact the evaporation test gives results, which are too low.

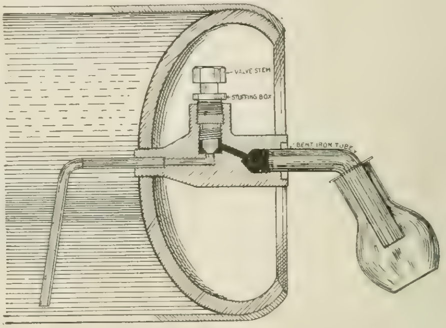


Fig. 2.

While this method of testing has become customary in the United States, the Linde method was used in Europe. The apparatus shown by Fig. 3 is used for the Linde test, and consists of a wider tube with a small hole near the center, the tube being drawn out at one end into a smaller tube which is closed in the bottom. The graduation was as indicated in the picture. In making the test the tube was supposed to be filled to the opening in the center, and the sample was permitted to evaporate in the open air. In operating this apparatus it would frequently occur that the ammonia would foam and boil up and part of the sample would run out of the opening. Since the time of evaporation was directed to be about three hours, the open vessel would permit much moisture to be attracted from the air. Besides, the graduation was incorrect because it did not take into consideration the difference in the specific gravities of the liquid ammonia, and of the residue left upon evaporation. For these reasons the results could not be accurate, but the degree of purity expected by European ice makers was not very

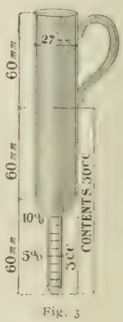


Fig. 3

[1] This paper was read at the first annual meeting of the American Institute of Chemical Engineers and will be published in full in the Transactions Vol. 1, 1908.

[1] Zeitschrift f. angew. Chemie, 1897, p. 224

great, an article leaving, upon evaporation, 1 per cent. of liquid residue being quite acceptable to them.[1]

Lange and Hertz[2] improved upon this apparatus and changed it to the form shown by Fig. 4. They omitted the overflow hole and replaced it by a mark indicating 49 cc. = 33.3 grams ammonia.

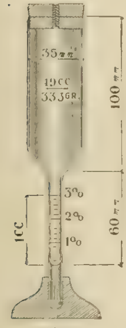


Fig. 4.

They increased the size of the sample from 30 cc. to 49 cc., and narrowed the tail end in order to permit a larger graduation. The latter they made proportionate to the specific gravities of the fluids to be measured. Finally they closed the tube with a cork during the time of evaporation, which was about three hours, letting the ammonia vapors escape through a narrow notch in the stopper. The result of tests made with this apparatus seemed to be sufficiently correct, since they worked with liquefied ammonia gas, leaving, upon evaporation, about 1 per cent. of non-volatile liquid. They also reported upon the quality of several German makes, finding that the average commercial article left, upon evaporation, about 1 per cent. of an oily substance. The nature of this residue of which they secured 185 cc. by evaporating 19.5 kilograms of commercial liquid ammonia was analyzed and ethyl alcohol, acetonitril, and pyridine were found in larger quantities, while the presence of smaller amounts of benzol, naphthalin, and carbonate of ammonium, and also lubricating oil could be established.

Since it was evident that both the Linde, and the Lange and Hertz test would show, upon evaporation, more residue than the ammonia really contained, the *Aktiengesellschaft für Chemische Industrie* in Mannheim caused Bunte and Eitner to design a new method which they published in 1897.[3] Their apparatus is represented in Fig. 5 and consists of a pipette having a strong glass body and a faucet on each end.

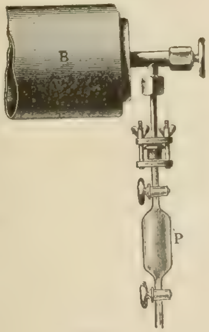


Fig 5

The sample was drawn under pressure, and its weight was ascertained. The pipette was then put in an upright position, the upper end connected with three caustic potash drying tubes, and by opening the upper faucet the sample was permitted to evaporate. After evaporation the pipette containing the residue was heated in an air bath to 70°–80° C. subjected to a current of air at that temperature and the weight of the von-volatile liquor was ascertained.

It is evident that the method favored the seller, since it generally would show a good test, the current of air carrying most of the residue out of the apparatus.

K. Urban[1] has improved upon this method, using an apparatus represented by Fig. 6. He graduated his pipette and heated the residue only to 30° C. to expel ammonia, but he did not use a current of air nor did he use caustic potash tubes. The specific gravity of the residue he determined by reading the volume on the graduation and ascertaining the weight. But he made an error by not considering the difference of specific gravities of air and ammonia gas, which was for his apparatus about thirty milligrams. Urban compared his method with other methods of testing then in us, and tabulated his results as shown in Table I.

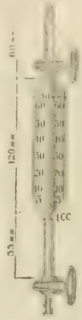


Fig. 6.

TABLE I.

A. BY URBAN'S METHOD.

45 cc. = 26.5 grams NH_3 left 0.25 gram = 0.94 per cent. residue.
45 cc. = 26.5 grams NH_3 left 0.25 gram = 0.94 per cent. residue.
45 cc. = 27.7 grams NH_3 left 0.25 gram = 0.91 per cent. residue.

B. BY LINDE'S METHOD.

30 cc. = 20.4 grams NH_3 left 0.534 gram = 2.61 per cent. residue.
30 cc. = 20.4 grams NH_3 left 0.530 gram = 2.59 per cent. residue.
30 cc. = 20.4 grams NH_3 left 0.535 gram = 2.62 per cent. residue.

C. BY THE LANGE AND HERTZ METHOD.

50 cc. = 34 grams NH_3 left 0.45 gram = 1.32 per cent. residue.
50 cc. = 34 grams NH_3 left 0.46 gram = 1.35 per cent. residue.
50 cc. = 34 grams NH_3 left 0.45 gram = 1.32 per cent. residue.
50 cc. = 34 grams NH_3 left 0.51 gram = 1.50 per cent. residue.
50 cc. = 34 grams NH_3 left 0.50 gram = 1.47 per cent. residue.

The last publication upon this subject has been by Lange and Heffter 1898[2] who reject the Linde method as being incorrect, and prove that the Bunte Eitner method is unreliable since its results are always too low. Then they compare the Urban and the Lange-Hertz methods, and prove by a number of experiments on samples of liquid ammonia containing known quantities of benzol,

[1] Lunge, "Coal, Tar and Ammonia," 4th German Edition, p. 161.
[2] *Zeits. f. angew. Chemie*, **1897**, p. 224.
[3] *Journal für Gasbeleuchtung*, **1897**, p. 174.

[1] *Chemiker Ztg.*, **1897**, p. 720.
[2] *Chemische Industrie*, **1898**, p. 2.

alcohol, pyridine, acetonitril, and also of mixtures of either two of these in equal parts, that Urban's method gives always too low results, while Lange-Hertz's method produces too high figures. In making the investigation they have operated with liquid ammonia leaving 0.2 per cent. residue upon evaporation, this being the best commercial ammonia which they could obtain. The results of their experiments are compiled in Table II.

TABLE II.

Kind and quantity of addition present.	Per cent.	Found. By Urban method. Per cent.	Found. By Lange and Hertz. Per cent.	Found. Per cent. of total present. By Urban. Per cent.	Found. Per cent. of total present. By Lange and Hertz. Per cent.
Benzol	1.5	0.99	1.7	66	113
"	1.5	0.75	1.5	50	100
"	1.5	1.13	1.5	75	100
"	1.5	0.77	1.0	51	67
"	1.5	0.76	1.0	51	67
Pyridine	1.0	0.65	1.2	65	120
"	1.0	0.70	1.1	70	110
Water	1.1	0.91	1.2	83	109
Alcohol	1.0	0.80	1.6	80	160
"	1.0	0.79	1.8	79	180
Alcohol and acetonitril	1.0	0.79	1.5	79	150
Alcohol and benzole	1.3	0.79	1.4	61	108
" " "	1.3	0.66	1.5	51	115
Alcohol and pyridine	1.0	1.01	1.5	101	150
" " "	1.0	1.02	1.6	102	160
Benzol and pyridine	1.0	0.80	0.9	80	90
" " "	1.0	0.66	1.1	66	110

They conclude that in Urban's method part of the impurities evaporate with the ammonia, and prove this theory by leading the vapors of 20 grams ammonia through a tube filled with pumice stone and cooled to —30° C., whereby the tube increased in weight by 26 milligrams.

They found that the amount of foreign substances evaporated with the ammonia varied with the nature of the substances. Benzol and pyridine escaped easily, alcohol and water with greater difficulty. Of the mixtures, alcohol and pyridine in equal parts did not seem to evaporate with the ammonia. However, with this statement I cannot agree. I have repeated this series of tests and the results are compiled in Table III. My figures show that a mixture of pyridine and alcohol evaporates just as well with ammonia as other substances. As a result of their investigation Lange and Heffter conclude that the results obtained by Urban's method are always too low while those obtained by the method of Lange-Hertz are too high, and they suggest to make both tests and take the average. This would seem quite arbitrary, but Lange-Heffter do not consider it worth while to look for a better method as long as no purer ammonia is offered in the market than an article leaving upon evaporation 0.2 per cent. residue.

TABLE III.

Liquid HN_3. Grams	Addition present. Kind.	Addition present. Grams.	Addition evaporated. By Urban. Per cent.	Addition evaporated. By Frerichs. Per cent.
98.5	Benzol	1.5	41	59
99.0	Pyridine	1.0	33	24
99.0	Alcohol	1.0	20	17
98.9	Water	1.1	17	11
99.0	½ Alcohol[1] ½ Pyridine	1.0	00	15
Used liquid NH_3 leaving, upon evaporation,			0.2	0.00

This was the aspect of the situation in Europe in 1898 and it would seem that the conditions are still the same at the present day.[2]

In the United States, the refrigerating industry has made much quicker progress than abroad. In the same measure as the ice plants multiplied and ice-making machinery became more perfect, the importance of the purity of the ammonia used in the plants became more evident because impure ammonia produced permanent gases in ice machines, and thereby decreased the efficiency of the plants.

As early as 1892, Hans von Strombeck, then in the employ of the De la Vergne Machine Company, published the analysis of six samples so called "anhydrous liquid ammonia 100 per cent." manufactured of different materials by different processes. He evaporated the samples in a flask connected with a long upright spiral condenser cooled with a refrigerating mixture, and obtained residues corresponding to the figures given in Table IV. The

TABLE IV.

	A. Per cent.	B. Per cent.	C. Per cent.	D. Per cent.	E. Per cent.	F. Per cent.
Ammonia by difference	98.976	96.984	98.220	99.792	99.321	99.180
Moisture	0.040	0.024	0.079	0.078	0.010	0.032
Colorless fluid	0.950	2.880	1.644	0.117	0.622	0.666
Hartshorn salt	0.030	0.099	0.049	0.004	0.043	0.087
Lubricant oil	0.004	0.006	0.005	0.009	0.004	0.035
Mineral matter	traces	0.007	0.003	traces	traces	traces
	100.000	100.000	100.000	100.000	100.000	100.000

colorless fluid he obtained by distillation of the crude residue under the reduced pressure of 200 mm. mercury, when it distilled at 106°–122° F. By repeated fractional distillation he could separate it into fractions, the boiling points of which corresponded with methyl alcohol, acetone, ethyl

[1] By an error in the first publication, THIS JOURNAL, **1**, 224, benzol has been printed instead of alcohol. Kindly correct.

[2] See H. Teichman's book on "Compressed Gases," p. 101, published 1908.

alcohol, and isopropyl alcohol. Believing only alcohol and acetones present as contaminations of commercial liquid ammonia, v. Strombeck proposed to purify it by distilling over metallic sodium. This process has been patented, and it was claimed that liquid ammonia 99.995 per cent. purity could be obtained by it.

v. Strombeck evidently overlooked benzol and pyridine among the impurities, and for that reason could not have obtained as pure ammonia as he thought. I have not been able to find that this process has been carried out on a large scale, but his investigation served as an incentive for other manufacturers to improve their product, and to furnish to the ice trade an article of such purity as they do now.

In the winter of 1897–'98 the writer had to rebuild the ammonia works of the Herf & Frerichs Chemical Company, and in order to control the working of the plant the larger of these two test apparati has been constructed. It aims to test the ammonia under such conditions as are prevailing in ice machines, inasmuch as the evaporation takes place under pressure, while the sample evaporated at a low temperature produced by a freezing mixture. The test apparatus was permanently connected with the plant, and a sample was taken from every 212 pounds ammonia manufactured. Apparati were changed and purifiers were added to the plant until the resulting ammonia upon evaporation in this apparatus did not leave any visible residue. In order to be still surer that the ammonia was pure an upright Liebig condenser cooled first by liquid ammonia, and subsequently by liquid carbonic acid, was connected with the flask containing the samples, and even in this case the evaporating ammonia did not leave any visible residue.

In one instance 235 consecutive samples, one from every 212 pounds of ammonia manufactured, representing altogether 49820 pounds of ammonia, were evaporated in the same flask leaving, upon evaporation, only 0.0187 gram of a residue containing moisture, iron rust, traces of ammonium carbonate, and a little lubricating oil.

The apparatus is illustrated by Figs. 7 and 8, and Fig. 9 shows the same apparatus without the Liebig condenser attached to a shipping cylinder containing liquefied ammonia gas.

"A" represents a cylinder containing liquid anhydrous ammonia. The test apparatus is attached to the valve "B," as indicated in the cut. Channel 4 terminates in the cross-channel 5, in the ends of which the valves 6 and 7 are located. By opening valves "B" and 6, connection with the outer air can be made through the opening 8, whereby any rust, etc., from the valve can be

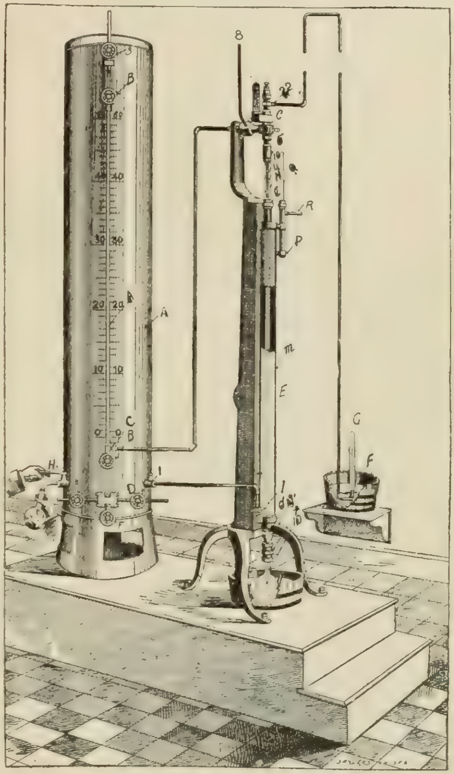


Fig. 7

blown off. By valve 7, connection can be established between channels 4 and 9, the latter extending by means of the tube 10 to the center of the flask 11, which is strong enough to withstand a pressure of 30 pounds, to the square inch.

The interior of the flask connects by way of channels 15, 16, 17, 18 with the automatic valve 19, and the spring 20 (the pressure of which can be regulated by the screw 21) holds the valve 19 in its seat, allowing only gases to escape through channel 22 if their tension is great enough to overcome the pressure of the spring. Valve 23 controls connection with the mercury gauge 24, which

indicates the pressure under which evaporation takes place.

In operating the apparatus it is attached to the cylinder of ammonia to be tested as indicated by the cut, and valve "B" is opened, all other valves of the apparatus being closed. By opening valve 6, some ammonia is blown off in order to remove

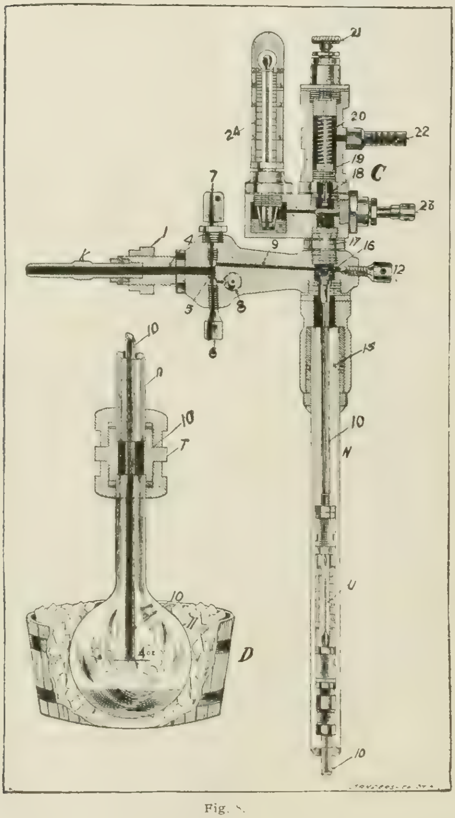


Fig. [illegible].

the rust or other foreign matter which may have gathered in valve B. If this has been accomplished, valve 6 is closed while valve 23 is opened and by operating valve 7, such quantities of ammonia are admitted into flask 11 as may be found convenient for the test.

The evaporation of the ammonia in flask 11 begins at once, and by means of the screw 21 the pressure under which the evaporation is to take place can be regulated to the desired degree, which is indicated by the mercury gauge 24. The evaporated ammonia escapes at 22.

If all the ammonia which has been admitted for a sample into flask 11 has been evaporated, a new sample can be filled into the same flask by operating valve 7, the apparatus being in the same condition in which it was at the beginning of the test, except that flask 11 now contains whatever impurities may have been left from the evaporation of the first sample. In this way a great many tests may be made in succession, and the entire contents of the cylinder can be evaporated in the small flask 11 in which remain, at the end of these tests, all the non-volatile impurities which have been contained in a very large amount of ammonia.

The smaller of these apparati has been constructed in more recent time; its particular object is to make the test independent from the moisture of the atmosphere. It is illustrated by Figs. 10 and 11, which explain themselves.

The apparatus is attached to the vessel containing the ammonia as shown in Fig. 10, and all rubber tubing is securely fastened with copper wire, wherever such joints occur. Ready for use the main valve on the ammonia cylinder is opened, and by opening the thumbscrew 1 some ammonia is blown off in order to remove rust and dirt which may have accumulated in the valve; this also will remove the small quantity of oil, which may have been used for lubricating the screw on the valve stem and which is always likely to be present in the interior of the valve.

If sufficient ammonia has been blown off to clear the valve, thumbscrew 1 is shut, and by opening thumbscrew 2 a sample of ammonia is admitted to the test bottle.

Care must be taken that ammonia is not admitted too quickly, otherwise the pressure in the bottle will become too great and either the bottle or the rubber connections are liable to burst. A Bunsen valve permits the ammonia vapor to escape, but prevents moisture of the air from entering the bottle.

The sample is permitted to evaporate while the apparatus remains attached to the cylinder. Evaporation may be hastened by dipping the graduated tail of the test bottle in cold water, whereby a gentle and steady boiling of the ammonia is kept up. Care should be taken not to dip the test bottle too deep into water, otherwise the ammonia may boil too rapidly and the bottle may explode

by excessive pressure. The slower the sample is evaporated the more reliable is the test. One hour and a half is a good time for evaporating 100 cc. ammonia in this apparatus. If evaporation is effected in much less time, the rapidly boiling ammonia will take with it some of the impurities, particularly hydrocarbons, if such are present and an inferior ammonia may show a good test.

During the evaporation, the tail of the test bottle will be heavily coated with ice, which will readily melt off after the sample of ammonia has evaporated by gently agitating the water in the surrounding vessel.

If 100 cc. are taken for the test, and if there remains some liquid in the tail of the test bottle, each subdivision in the scale indicates 1/10 of 1 per cent. by volume in the ammonia.

A second and third sample can be evaporated in the same bottle without removing the apparatus from the cylinder and this may be continued until the entire contents of a cylinder has been evaporated, in which case the test bottle will contain all of the impurities which have been contained in the entire cylinder.

Before taking a new test some ammonia is blown off by opening thumbscrew 1 in order to remove as much as possible the traces of oil which may have seeped into the valve from the lubricant used for the valve stem.

If more accurate results are desired the Bunsen valve on the side outlet of the flask is replaced by a bent glass tube leading the ammonia gas into water where it is absorbed. A Bunsen valve attached to the end of the glass tube, which dips into the water, prevents the water from backing up into the test flask. The amount of the ammonia used for the test is then ascertained by titrating the solution of ammonia in water, and the amount of residue left upon evaporation is determined by weighing the test flask before and after the test on a chemical balance. Care must be taken to close the outlets of the flask, and to have constant temperatures while weighing, also to have the flask entirely filled with ammonia gas in order to exclude errors resulting from the difference in the specific gravities of air and ammonia gas.

Liquefied ammonia gas seems to be an absorbent for permanent gases. They may be determined with the aid of this apparatus by collecting them in a eudiometer filled with water after the ammonia gas has been absorbed in the water of a pneumatic trough. If this be done care should be taken to use

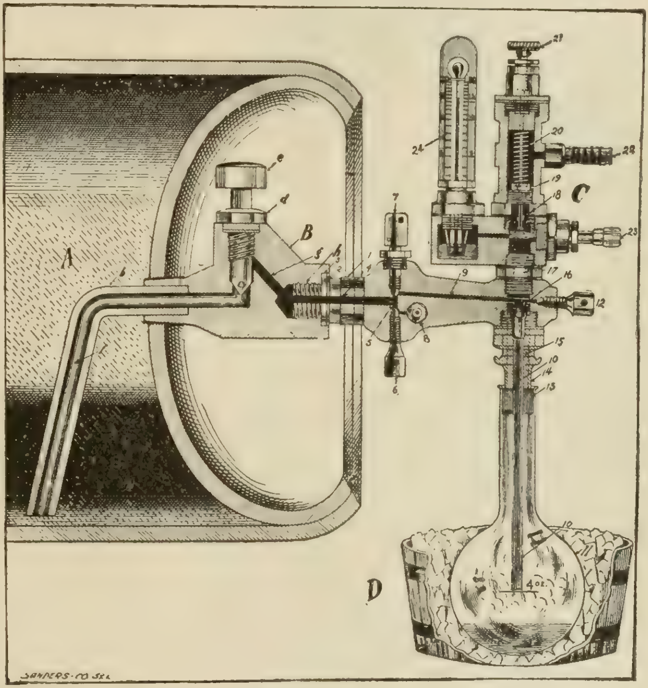


Fig. 9.

water which has been freed from air by protracted boiling since ammonia gas disengages air from water which is saturated with it.

Small quantities of alcohols and water can be determined in liquid ammonia by treating it with metallic sodium and measuring the quantity of hydrogen evolved. The mode of operation is as follows:

Sufficient sodium is inserted into the test flask, which is then connected with the test valve and provided with the extension tube and eudiometer

filled with water and standing in a pneumatic trough. Some liquid ammonia is admitted which dissolves the sodium to a dark blue liquid, the evaporating ammonia expelling the air from the

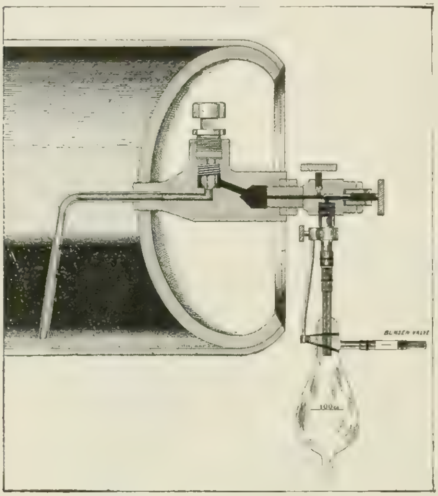


Fig. 10.

flask. If the ammonia has evaporated to 1 cc., and if the air has been expelled the glass tube is inserted into the pneumatic trough and under the opening of the eudiometer and ammonia for the sample is admitted. Hydrogen is evolved at once as a result of the decomposition of water and alcohols contained in the ammonia. If the sample has evaporated to 1 cc. the volume of hydrogen is measured and the amount of ammonia absorbed in the water of the pneumatic trough is determined by titrating, giving the data for calculation. The results obtained by this method are a little too high because ammonia is decomposed slowly by sodium to sodium amide and hydrogen. But it would seem that this secondary reaction is so slow that the result is only slightly affected.

With this apparatus, a series of tests has been made with a view of ascertaining its accuracy in determining the various impurities, which are most frequently contained in commercial liquefied ammonia gas.

As a basis, liquid ammonia was used which had been manufactured in the regular run of the works from sulphate of ammonia previously purified from all volatile carbon compounds, and in the manufacture of the product great care was taken that all the moisture was eliminated. For this reason it was certain that bodies like benzol, pyridine, alcohols, and other carbon compounds could not be present, and the limit of water was ascertained by analysis to be less than 2 milligrams in 100 grams of liquid ammonia. The determination of water was made by adding an ammoniacal solution of metallic sodium to the liquid ammonia to be analyzed, and collecting the hydrogen, which was evolved by the reaction of the sodium upon the water in the sample. 100 grams of the liquid ammonia treated in this way produced 2.4 cc. hydrogen. If all the hydrogen had been produced from water 2 milligrams of water must have been present, but it is well known that ammonia itself decomposes slowly with sodium into sodium amide and hydrogen and for this reason part of the hydrogen may have come from the ammonia, in which case the water present would be less than 0.002 per cent. As a fact, I will state that about one-half of the hydrogen was developed rapidly right after the sodium solution had been added, while the balance accumulated from minute bubbles during the time of evaporation of the entire hundred grams of the liquid ammonia, and for this reason it is quite possible that the second half comes from decomposition of ammonia. Therefore, under no circumstances could more than 0.002 per cent. water

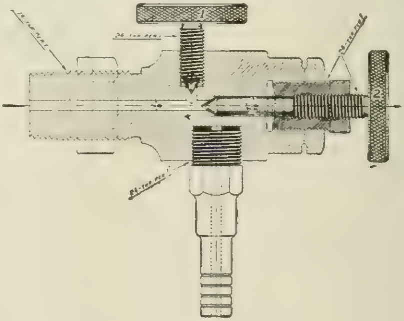


Fig. 11.

be present, and it is possible that the quantity of water in the sample was not more than half of that amount. Table V gives the result of five tests made with this ammonia in the smaller of the two apparati and from the uniformity of the results and the insignificance of the residue the purity of the liquid ammonia is evident.

TABLE V.

80 grams liquid NH_3 left after evaporation 0.003 gram.
160 grams liquid NH_3 left after evaporation 0.003 gram.
240 grams liquid NH_3 left after evaporation 0.003 gram.
320 grams liquid NH_3 left after evaporation 0.005 gram.
400 grams liquid NH_3 left after evaporation 0.007 gram.
Residue from evaporation 0.00175 per cent.
Ammonia by difference 99.99825 per cent.
The residue consisted of iron oxide shown by potassium ferrocyanide, and little lubricating oil.

With ammonia of this purity, the experiments of Lange and Heffter have been repeated. The results I have given in Table III. In addition a series of samples containing variable, but known quantities of benzol, pyridine, alcohol, and water have been evaporated in the new apparatus, and the residues left after evaporation have been ascertained as given in Table VI.

TABLE VI.

Evaporated with liquid NH_3	Benzol. Gram.	Pyridine. Gram.	½ Alcohol. ½ pyridine. Gram.	Alcohol. Gram	Water. Gram.
	0.527	0.652	0.966	0.676	0.673
First 100 cc.	0.258	0.142	0.142	0.099	0.077
Second 100 cc.	0.178	0.135	0.131	0.089	0.066
Third 100 cc.	0.077	0.084	0.117	0.077	0.061
With 300 cc. evaporated grams	0.513	0.361	0.390	0.265	0.204
With 300 cc. evaporated per cent.	97	55	40	39	30

From this table it is evident that the quantities of the additions which evaporate with the ammonia decrease if less of the addition is present.

Table VII shows the same results differently arranged. It gives the proportion of the addition evaporated with the ammonia to the total amount of the addition present before the evaporation, and a marked difference is observed between benzol on the one side and pyridine, alcohol, and water on the other. While the percentage evaporated seems to be the same for varying quantities of the addition present in the case of pyridine, alcohol and water, it increases rapidly with a decreasing addition of benzol.

TABLE VII.

Benzol		Pyridine		Alcohol		Water	
present, per cent. of ammonia.	evap., per cent of benzol.	present, per cent. of ammonia.	evap., per cent. of pyridine	present, per cent of ammonia.	evap., per cent. of alcohol.	present, per cent. of ammonia	evap., per cent. of water.
1.50	59	1.00	24	1.00	17	1.10	11
0.65	49	0.81	22	0.84	14	0.84	11
0.34	66	0.64	26	0.72	15	0.75	11
0.11	84	0.47	22	0.61	16	0.66	11

The limit of accuracy of this mode of testing has been ascertained in a special series of experiments as follows:

For water to 0.002 gram in 100 grams ammonia.
For alcohol to 0.006 gram in 100 grams ammonia.
For pyridine to 0.009 gram in 100 grams ammonia.
For benzol to 0.110 gram in 100 grams ammonia.

In other words, 100 cc. samples of liquid ammonia containing these additions, leave, upon evaporation, a visible residue of at least one milligram.

HERF AND FRERICHS CHEMICAL CO.
ST. LOUIS, MO.

NOTES AND CORRESPONDENCE.

RECENT LEGISLATION RELATIVE TO EXPLOSIVES IN THE MAIL AND TRANSPORTATION.

The act to codify, revise, and amend the penal laws of the United States published as (Public-No. 350) and (S. 2982), approved March 4, 1909 and taking effect January 1, 1910, provides under offenses against the Postal Service.

Sec. 217. All kinds of poison, and all articles and compositions containing poison, and all poisonous animals, insects, and reptiles, and explosives of all kinds, and inflammable materials, and infernal machines, and mechanical, chemical, or other devices or compositions which may ignite or explode, and all disease germs or scabs, and all other natural or artificial articles, compositions, or materials of whatever kind which may kill, or in any wise hurt, harm, or injure another, or damage, deface, or otherwise injure the mails or other property, whether sealed as first-class matter or not, are hereby declared to be nonmailable matter, and shall not be conveyed in the mails or delivered from any post-office or station thereof, nor by any letter carrier; but the Postmaster-General may permit the transmission in the mails, under such rules and regulations as he shall prescribe as to the preparation and packing, of any articles hereinbefore described which are not outwardly or of their own force dangerous or injurious to life, health, or property: Provided, That all spirituous, vinous, malted, fermented, or other intoxicating liquors of any kind, are hereby declared to be nonmailable and shall not be deposited in or carried through the mails. Whoever shall knowingly deposit or cause to be deposited for mailing or delivering, or shall knowingly cause to be delivered by mail according to the direction thereon, or at any place at which it is directed to be delivered by the person to whom it is addressed, anything declared by this section to be nonmailable, unless in accordance with the rules and regulations hereby authorized to be prescribed by the Postmaster-General, shall be fined not more than one thousand dollars, or imprisoned not more than two years, or both; and whoever shall knowingly deposit or cause to be deposited for mailing or delivery, or shall knowingly cause to be delivered by mail according to the direction thereon, or at any place to which it is directed to be delivered by the person to whom it is addressed, anything declared by this section to be nonmailable, whether transmitted in accordance with the rules and regulations authorized to be prescribed by the Postmaster-General or not, with the design, intent, or purpose to kill, or in anywise hurt, harm, or injure another, or damage, deface, or otherwise injure the mails or other property, shall be fined not more than five thousand dollars, or imprisoned not more than ten years or both

It provides under the offenses against Foreign and Interstate Commerce.

Sec. 232. It shall be unlawful to transport, carry, or convey any dynamite, gunpowder, or other explosive, between a place in a foreign country and a place within or subject to the jurisdiction of the United States, or between a place in any State, Territory, or District of the United States, or place noncontiguous to but subject to the jurisdiction thereof, and a place in any other State, Territory, or District of the United States, or place noncontiguous to but subject to the jurisdiction thereof, on any vessel or vehicle of any description operated by a common carrier, which vessel or vehicle is carrying passengers for hire: Provided, That it shall be lawful to transport on any such vessel or vehicle small arms ammunition in any quantity, and such fuses, torpedoes, rockets, or other signal devices, as may be essential to promote safety in operation, and properly packed and marked samples of explosives for laboratory examination, not exceeding a net weight of one-half pound each, and not exceeding twenty samples at one time in a single vessel or vehicle which is intended for the transportation of passengers for hire: Provided further, That nothing in this section shall be construed to prevent the transportation of military or naval forces with their accompanying munitions of war on passenger equipment vessels or vehicles.

Sec. 233. The Interstate Commerce Commission shall formulate regulations for the safe transportation of explosives, which shall be binding upon all common carriers engaged in interstate or foreign commerce which transport explosives by land. Said commission, of its own motion, or upon application made by any interested party, may make changes or modifications in such regulations, made desirable by new information or altered conditions. Such regulations shall be in accord with the best known practicable means for securing safety in transit, covering the packing, marking, loading, handling while in transit, and the precautions necessary to determine whether the material when offered is in proper condition to transport. Such regulations, as well as all changes or modifications thereof, shall take effect ninety days after their formulation and publication by said commission and shall be in effect until reversed, set aside, or modified.

Sec. 234. It shall be unlawful to transport, carry, or convey, liquid nitroglycerin, fulminate in bulk in dry condition, or other like explosive, between a place in a foreign country and a place within or subject to the jurisdiction of the United States, or between a place in one State, Territory, or District of the United States, or place noncontiguous to but subject to the jurisdiction thereof, and a place in any other State, Territory, or District of the United States, or place noncontiguous to but subject to the jurisdiction thereof, on any vessel or vehicle of any description operated by a common carrier in the transportation of passengers or articles of commerce by land or water.

Sec. 235. Every package containing explosives or other dangerous articles when presented to a common carrier for shipment shall have plainly marked on the outside thereof the contents thereof; and it shall be unlawful for any person to deliver, or cause to be delivered, to any common carrier engaged in interstate or foreign commerce by land or water, for interstate or foreign transportation, or to carry upon any vessel or vehicle engaged in interstate or foreign transportation, any explosive, or other dangerous article, under any false or deceptive marking, description, invoice, shipping order, or other declaration, or without informing the agent of such carrier of the true character thereof, at or before the time such delivery or carriage is made. Whoever shall knowingly violate, or cause to be violated, any provision of this section, or of the three sections last preceding, or any regulation made by the Interstate Commerce Commission in pursuance thereof, shall be fined not more than two thousand dollars, or imprisoned not more than eighteen months, or both.

Sec. 236. When the death or bodily injury of any person is caused by the explosion of any article named in the four sections last preceding, while the same is being placed upon any vessel or vehicle to be transported in violation thereof, or while the same is being so transported, or while the same is being removed from such vessel or vehicle, the person knowingly placing, or aiding or permitting the placing, of such articles upon any such vessel or vehicle, to be so transported, shall be imprisoned not more than ten years.

Section 341, under Repealing Provisions, repeals the act entitled "An Act to promote the safe transportation in interstate commerce of explosives and other dangerous articles, and to provide penalties for its violation," approved May thirtieth, nineteen hundred and eight.

Charles E. Munroe.

METHOD OF ANALYSIS FOR MASSECUITES AND MOLASSES.

The analysis of massecuites and molasses is one of the most difficult problems in sugar analysis, for with most methods, even a moderate speed can be attained only with more or less loss in accuracy. In the course of analysis of about two thousand samples by the author, several different methods were tried and found unsatisfactory, and finally the following modification of one of Spencer's methods[1] was devised.

The use of a refractometer for determining the density, or Brix, of the sample is of course preferable to the method described here, but in laboratories where a refractometer is not available, it is hoped this method will be found of use.

Weigh out 125 grams of the sample in an ordinary nickel tare, add a little hot water—20 or 25 cc. if the tare will hold that much without danger of slopping over—and stir thoroughly with a small pestle, made by heating and flattening the end of a heavy glass rod. A molasses will thus be readily thinned down so it can be poured into a flask. A massecuite must be stirred until all lumps are broken up and the molasses adhering to the sugar crystals is all dissolved. The contents of the tare can then be poured into a flask and the tare washed out, using a second portion of hot water if necessary. The flask should be a 500 cc. one, graduated, with as wide a neck as possible. After the contents of the tare are all washed into the flask, fill the flask half full of water and shake till all the contents are dissolved. In a factory laboratory where several samples are run at one time, the samples can all be transferred into the flasks and turned over to the helper to dissolve.

After the sample is completely dissolved, fill the flask to the mark with the coldest water available, and shake thoroughly. Unless a large amount of hot water has been used in dissolving the sample, and transferring it to the flask, the diluted sample will be ready for analysis without further

[1] Spencer's "Handbook for Sugar Manufacturers," p. 147.

cooling. If the temperature of the solution is over 30° C., the flask should be cooled in a stream of cold water from the hydrant, and the solution made up to the mark again. Transfer the solution to a 1¼ x 15″ glass cylinder and note the Brix with an ordinary Brix spindle, and the temperature with a Centigrade thermometer. The apparent degree

TABLE SHOWING BRIX OF MATERIALS DILUTED 125 GRAMS TO 500 CC.

Note the Brix and temperature of the diluted solution, and read the Brix of the original material at the intersection of the horizontal or vertical columns corresponding to the Brix and temperature as noted.

Brix.	18° C.	19°.	20°.	21°.	22°.	23°.	24°.	25°.	26°.	27°.	28°.	29°.
19.0	82.12	82.38	82.73	83.03	83.33	83.63	83.89	84.19	84.49	84.80	85.10	85.40
19.1	82.59	82.84	83.19	83.49	83.80	84.10	84.36	84.66	84.96	85.26	85.56	85.87
19.2	83.05	83.51	83.66	83.96	84.26	84.56	84.62	85.13	85.43	85.73	86.03	86.34
19.3	83.52	83.78	84.12	84.43	84.73	85.02	85.29	85.59	85.90	86.20	86.50	86.80
19.4	83.99	84.25	84.59	84.89	85.20	85.51	85.76	86.06	86.36	86.67	86.97	87.27
19.5	84.45	84.71	85.06	85.36	85.66	85.97	86.23	86.53	86.83	87.13	87.44	87.74
19.6	84.92	85.18	85.53	85.83	86.13	86.43	86.69	87.00	87.30	87.60	87.91	88.21
19.7	85.39	85.65	85.99	86.30	86.60	86.90	87.16	87.47	87.78	88.07	88.39	88.68
19.8	85.86	86.12	86.46	86.77	87.07	87.37	87.63	87.93	88.24	88.54	88.84	89.15
19.9	86.32	86.58	86.93	87.23	87.54	87.84	88.10	88.40	88.71	89.01	89.31	89.62
20.0	86.79	87.05	87.40	87.70	88.01	88.31	88.57	88.87	89.18	89.48	89.78	90.09
20.1	87.26	87.52	87.87	88.17	88.47	88.78	89.04	89.34	89.64	89.95	90.25	90.56
20.2	87.73	87.99	88.34	88.64	88.94	89.25	89.51	89.81	90.11	90.42	90.72	91.02
20.3	88.20	88.46	88.81	89.10	89.41	89.72	89.98	90.29	90.59	90.89	91.20	91.50
20.4	88.67	88.93	89.28	89.59	89.89	90.19	90.45	90.76	91.06	91.36	91.67	91.97
20.5	89.14	89.40	89.75	90.06	90.36	90.66	90.92	91.23	91.53	91.84	92.14	92.44
20.6	89.62	89.88	90.22	90.53	90.83	91.14	91.40	91.70	92.00	92.31	92.61	92.92
20.7	90.09	90.35	90.70	91.00	91.30	91.61	91.87	92.17	92.48	92.78	93.09	93.39
20.8	90.56	90.82	91.17	91.47	91.78	92.08	92.34	92.65	92.95	93.25	93.56	93.86
20.9	91.03	91.29	91.64	91.94	92.25	92.55	92.81	93.12	93.42	93.72	94.03	94.34
21.0	91.50	91.77	92.11	92.42	92.72	93.03	93.29	93.59	93.90	94.20	94.51	94.81
21.1	91.98	92.24	92.59	92.89	93.29	93.50	93.76	94.07	94.37	94.68	94.98	95.29
21.2	92.45	92.71	93.06	93.37	93.67	93.98	94.24	94.54	94.85	95.15	95.46	95.76
21.3	92.93	93.19	93.53	93.84	94.14	94.45	94.71	95.02	95.32	95.63	95.93	96.24
21.4	93.40	93.66	94.01	94.31	94.62	94.92	95.17	95.49	95.80	96.10	96.41	96.71
21.5	93.87	94.14	94.48	94.79	95.10	95.40	95.66	95.97	96.27	96.58	96.88	97.19
21.6	94.36	94.61	94.96	95.27	95.57	95.88	96.13	96.44	96.75	97.05	97.36	97.66
21.7	94.83	95.09	95.44	95.74	96.05	96.35	96.61	96.92	97.23	97.53	97.84	98.14
21.8	95.30	95.56	95.91	96.22	96.52	96.83	97.09	97.40	97.70	98.01	98.31	98.62
21.9	95.78	96.04	96.39	96.69	97.00	97.31	97.57	97.87	98.18	98.48	98.79	99.10
22.0	96.25	96.52	96.87	97.17	97.48	97.78	98.04	98.35	98.66	98.96	99.27	99.57
22.1	96.73	96.99	97.34	97.65	97.96	98.26	98.52	98.83	99.14	99.44	99.75	...
22.2	97.21	97.47	97.82	98.13	98.43	98.74	99.00	99.31	99.61	...	...	...
22.3	97.69	97.95	98.30	98.61	98.91	99.22	99.48	...	...	...	...	...
22.4	98.16	98.43	98.78	99.08	99.39	99.70	...	...	...	...	...	...
22.5	98.64	98.91	99.26	99.56	...	...	...	...	...	...	...	...
22.6	99.12	99.38	99.74	...	...	...	...	...	...	...	...	...
22.7	99.60	99.86	...	...	...	...	...	...	...	...	...	...

Brix of the original sample can then be obtained from the following formula:

$$\text{Apparent degree Brix} = \frac{S \times B \times V}{W}$$

when B = degree Brix of the diluted sample, corrected for temperature;

S = specific gravity, corresponding to the Brix before correcting for temperature;

V = volume of the solution;

W = weight of material used.

Having used the quantities specified, this formula becomes:

$$\text{Apparent degree Brix} = \frac{S \times B \times 500}{125} = S \times B \times 4.$$

Since this solution contains 0.25 gram of the original sample in each cc., it is only necessary to fill a Spencer pipette to the zero mark, thus measuring out 52.096 cc., to obtain a half normal weight of the original sample for polarization. This is transferred to a 100 cc. flask, lead acetate added to clarify, filled to the mark, filtered and polarized.

To avoid repeated calculation, in the following table the apparent density or degree Brix of the original sample has been calculated for a sufficient range of temperature and Brix of diluted sample to include all ordinary practice.

By using this table for the Brix, and 52.096 cc. of the diluted sample for the sucrose, the analysis of massecuites and molasses may be made with a very satisfactory degree of speed and accuracy.

G. A. ROUSH.

THE VALUATION OF INSOLUBLE PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

It is customary in the majority of states having laws regulating the sale of fertilizers, to place a value on the ingredients that enter into the composition of the fertilizers. These values are expressed as either cost per unit (20 lbs.) or cost per pound, and where the value has been stated as cost per unit, the cost per pound has been calculated and used in the accompanying table. In some states no valuation is made on insoluble phosphoric acid, and in other states a value is placed on insoluble phosphoric acid irrespective of its source; *i. e.*, whether or not it is derived from rock phosphate or from bone.

In the manufacture of mixed fertilizers, the phosphoric acid may be derived from either well-made acid phosphate (low insoluble phosphoric acid), badly made acid phosphate (high insoluble phosphoric acid) or tankage or guano con-

taining bone, or a combination of any of these. In mixtures containing badly made acid phosphate, or tankage or guano containing bone, the insoluble phosphoric acid will be high.

CENTS PER POUND FOR PHOSPHORIC ACID.

	Insoluble from bone.	Insoluble from rock.	In tankage.	Insoluble in mixed fertz	Insoluble.	Insoluble in fertz. containing N.	In bone meal.
Pennsylvania	2	$1\frac{1}{2}$	3	..	..	..	3
Maryland	..	1	3	2	..	..	3
Florida	..	..	..	..	1	..	..
Maine, Massachusetts, New Jersey, Rhode Island, Vermont, Connecticut, New York	..	..	4	2	..	..	4
Michigan	..	..	..	..	..	2	4
Georgia	..	..	..	..	..	..	$3\frac{3}{4}$
Texas	..	..	4	..	..	..	4
Louisiana	..	..	1.09	..	..	..	4

It will be seen by glancing at the accompanying table, that in those states in which a value is placed on insoluble phosphoric acid in mixed fertilizers, this value is invariably lower than the value placed on bone in tankages; that is, those manufactures using tankage containing bone in their mixed fertilizers do not obtain a correct valuation, but are placed in the same class with those manufacturers that use badly made acid phosphate. The present method of determining insoluble phosphoric acid does not differentiate between that derived from phosphate rock and that derived from bone. The following method has been worked out and found satisfactory for determining approximately the amount of insoluble phosphoric acid, from each source, present in a mixed fertilizer containing both.

This method depends upon the microscopical examination of the fertilizer, and therefore its accuracy is limited to that usually obtained in a quantitative determination by means of the microscope. The samples are mounted in water in the usual manner by rubbing down between the cover glass and slide. The samples are ground to pass a 40-mesh sieve.

On viewing a sample of bone tankage, by means of a microscope magnifying 150 diameters, the organic fibrous matter is seen to be interspersed with particles of bone. The small pieces of bone are translucent, with a pearly luster. The larger pieces of bone only show this luster on the edges.

The examination of acid phosphate shows it as a uniform, non-crystalline mass, not translucent.

In examining a mixed fertilizer, the method that has been found most convenient is as follows: The sample is mixed, quartered down to about 4 oz., ground to pass a 40-mesh sieve and placed in a stoppered bottle. For a preliminary examination, a small portion is mounted in water and examined under a microscope. The presence or absence of bone is immediately shown. If bone is found to be present the fertilizer may be further examined to determine the proportions of insoluble phosphoric acid from bone and acid phosphate as follows: Two grams of the ground fertilizer are treated according to the official method of the A. O. A. C. for the determination of insoluble phosphoric acid in mixed fertilizers. However, after washing with 250 cc. of distilled water, instead of placing the filter paper with the fertilizer into 100 cc. of ammonium citrate solution, scrape the washed fertilizer from the paper and proceed as usual, thus eliminating the paper pulp and facilitating the following examination: In filtering the insoluble matter, use a filter paper, the apex of which is supported by either a platinum or parchment cone. After filtering and washing, scrape the insoluble residue from the filter paper, mix, and examine under a microscope. The insoluple phosphate rock can readily be distinguished from the accompanying bone and organic matter. By comparing it with standard mixtures, a fair approximation of the proportion of the insoluble phosphoric acid derived from the acid phosphate may be obtained. By determining the total insoluble in the usual manner the insoluble phosphoric acid from bone may be obtained.

Using the above method, a more nearly accurate valuation of mixed fertilizers can be obtained. It has been my experience that mixed fertilizers made from tankage and well-made acid phosphate will rarely run over 0.5 per cent. of insoluble phosphate rock, and will, in the majority of cases, run below this figure. If, on finally examining a fertilizer, only a small quantity of insoluble phosphate rock is present, the chemist would come very close to the truth if he used the value 0.5 per cent. for insoluble phosphate rock. When it is considered that some fertilizers containing tankage run as high as 4 per cent. insoluble phosphoric acid, the fact can readily be seen that the correct valuation of the insoluble phosphoric acid in a mixed fertilizer is of great importance to the manufacturer using tankage.

R. H. FASH.

SWIFT & COMPANY,
CHEMICAL LABORATORY,
FT WORTH, TEXAS.

A SYSTEM OF RECORDS FOR THE SCIENTIFIC WORK OF A MANUFACTURING PHARMACEUTICAL ESTABLISHMENT.

The system of reports and records here described is the outgrowth of several attempts to keep complete and convenient records of scientific work. As it became necessary to abandon these systems on account of the growth and branching out of the work it was determined to adopt, if possible, a system which would care for the work of a growing department indefinitely. This requirement seems to be met by the present system, which by modifying certain details, could be adapted to the needs of many laboratories engaged in other lines of work. In order to understand some of the difficulties encountered, and also some of the details of the system under consideration, it will be necessary to present the organization of the scientific work for which the system was designed. This is shown in the following diagram:

Subdivision of Chemistry and Biology.

- I. Department of Chemistry.
  - *a.* Routine.
    - (1) Examination of crude materials which can be controlled chemically.
    - (2) Assaying drugs and finished products, including chemical control of manufacturing processes.
  - *b.* Research.
- II. Department of Botany—Inspection of crude vegetable drugs and botanical research.

III. Department of Pharmacology and Bacteriology—
Testing of crude materials and finished products on animals and bacteria.
Pharmacologic research.
IV. Library and Scientific Records.
V. Care of Scientific Apparatus and Materials.

Technical supervision of manufacturing and pharmaceutical development form two separate subdivisions and are not provided for in this system of records; however, the subdivision of chemistry and biology must by means of reports keep in close touch with these, as well as with the subdivision of manufacturing (including the stock department), and with the purchasing department. All crude materials, from 1500 to 2000 in number, must be examined and, if approved, reported to the stock department by means of a serially numbered slip to be attached to each package; if rejected, a different form of slip is sent to the stock department, and a report must go to the manufacturing office and to the purchasing department. Many samples of materials are received by the purchasing department which must be examined and reported upon.

Some crude materials and samples are examined by two or more departments, for instance many crude vegetable drugs are examined by the botanical department and assayed by the routine chemical department, yet to avoid confusion only one report must go to the purchasing department. In addition to the work on crude materials many finished preparations are assayed and standardized, and manufacturing processes are controlled by chemical tests. Various lines of research are also carried on.

Complete and permanent records of all of this work must be kept in such a manner as to be readily accessible, at all times, to the director of the scientific work. Each worker should also have a record of his own work for convenient reference.

To meet these requirements, with a minimum amount of clerical work, this system was devised. Nine permanent loose-leaf records are provided:

1. Crude Vegetable Drugs.
2. Other Crude Materials.
3. Chemical Research.
4. Chemical Routine.
5. Botany.
6. Pharmacology and Bacteriology.
7. Manufacturing Losses.
8. Standard Methods of Analysis.
9. Index to Scientific Literature.

Records 1 and 2 are simply lists of lots and samples of crude materials received, each of which is given a serial number by an automatic numbering machine, and has recorded its source, disposition, and the name of the examiner. A page (Fig. 1) is devoted to each crude material, the pages are arranged alphabetically and at the top of each page the requirements for the material in question and references to the "Standard Methods of Analysis" are written. These lists make it easy to determine, the customary source for any crude material, the source of each individual lot, the number of lots received in any specified time, the person responsible for each lot, and whether or not samples have been examined to which subsequent lots from the same source should conform. The entries in these records are made by the person who examines the crude material.

Each worker is supplied with a spring back binder which will hold from one to seventy-five loose leaf sheets (Fig. 2) $4\frac{1}{2}$ x 8 inches in size, one of which is properly headed and inserted in the binder for each subject assigned for work. On the back of this sheet a record of weighings, outline of calculations, and other details are placed, and when the final results are obtained all matter essential to the permanent records is written on the front of the blank; several modifica-


Article
Requirements
Date 19 | Number | Source | Remarks | Ex. by

Fig. 1.

tions of this report blank, of uniform size, are in use for special lines of work. The reports when finished are taken out of the binder, so that the remaining sheets serve as memoranda of work to be completed. The finished reports are submitted to the head of the department in which the work was done and are then transmitted with the proper notations to the librarian, who enters in the permanent records the data appearing on the front of the report. This

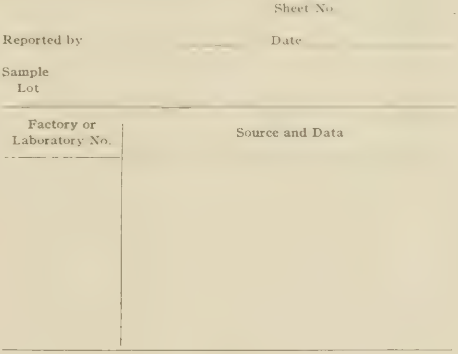

Sheet No.
Reported by
Date
Sample
Lot
Factory or Laboratory No. | Source and Data

Fig. 2.

entry is made by means of a special typewriter with 96 characters which make it possible to write chemical formulas and other frequently used chemical signs. In the permanent records a page (Fig. 3) is assigned to each subject, and when filled another is inserted so that no matter how voluminous the records may become, all information upon one subject remains together and its alphabetical arrangement is never disturbed. Modifications of this record blank

with headings printed in to facilitate the tabulation of retain data are also in use.

After this entry is made and verified the original report is returned to the author, who files it in alphabetical order in a binder provided for this purpose; this file constitutes his individual record and in it all reports are kept for a reasonable length of time, those over one year old being taken out and stored in boxes.

The blank ends of these sheets serve to carry memoranda to the librarian directing the sending of reports to any other divisions or departments of the business, and these reports are made out at the time that the entry in the permanent record is made. Materials examined by two or more departments are reported upon to the department chiefly concerned in their examination; all reports are then embodied in the report from this department.

Taking the data from the reports on assayed drugs and the standardized preparations made from them, the head of the routine chemical department keeps an interesting record (No. 7) showing the manufacturing losses. A record of each preparation is kept on a sheet of squared paper, the abscissae representing the per cent. of active principles in the drug, and the ordinates the ratio of the yield of finished preparation to the amount of crude material used.

Sheet No.____________

	Date	

Fig. 3.

A line is drawn showing the yield of finished preparation which would be obtained from crude materials of the various strengths if there was no loss in manufacturing. Each lot of the preparation manufactured is represented by a point which falls somewhat below this line, and after a sufficient number of points are fixed, a line representing the average losses in manufacturing can be drawn. Any carelessness in manufacturing or any improvement in process is then readily shown.

Confusion in the records and in the laboratories is avoided by giving to everything which is made the subject of laboratory investigation a distinctive number, which is used on all reports and records. Several series of numbers are in use, but the different lines of work are so well defined that no confusion results.

Aside from records 1, 2, and 7, and the numbered slips for the stock department, it is only necessary for the laboratory worker to make one report on each subject, which serves as a laboratory memorandum, and from which all necessary reports and records are made without further attention on his part. All reports sent to the purchasing department in regard to crude materials are filed there and form a convenient permanent record for that department.

Records 8 and 9 are kept on the regular record blank (Fig. 2). Record 8 gives methods devised in our laboratories or selected from other sources. The index of scientific literature is kept by the librarian and includes only those articles which have a direct bearing on our lines of work. All journals in the library are represented in the index, the articles being marked, and cross references indicated by members on the scientific staff. Articles treating on the same subject are indexed on the same sheet under a suitable heading and copious cross references are made so that the information indexed is easily found. In all the records cross references are inserted wherever they seem to be of value.

FRANK R. ELDRED.

DEPARTMENT OF CHEMISTRY,
ELI LILLY & CO.

THE EFFECT OF THE PROPOSED TARIFF BILL ON AMERICAN CHEMICALS.

It is interesting to study the tariff bill as proposed by the Ways and Means Committee in conjunction with the hearings and briefs submitted by interested manufacturers of chemical with a view to determining to what extent the mind of the legislator is influenced by the manufacturer's arguments.

Again, it is of interest in comparing the proposed tariff bill as submitted by the Finance Committee of the Senate with that of the House to observe the diversity of opinion as to what will best serve this country's good, for such, of course, is the purpose of the act which reads, "to provide revenue, equalize duties, and encourage the industries of the U. S., and for other purposes," and one is inclined to ask what motive or reason can be assigned for such contradictory action by the two bodies of legislation.

One is satisfied, after a perusal of the bills and hearings and observing the hoards of manufacturers, importers and others crowding the hotels of Washington and hounding the congressmen for favor, that Hancock was right when he said that the tariff is a "local question": each for his own interest.

The methods pursued by those interested in holding the present duty or increasing the duty on their manufactured product or getting their raw materials put on the free list, vary greatly. Some appeared in person before the Ways and Means Committee; others preferred to send in briefs, thus avoiding the cross-questioning of the committee; some disregarded entirely the Ways and Means Committee and worked with the Senate Finance Committee. If one had in his favor the captious phrase "for the benefit of the farmer," he had all the Representatives with him.

As tariff revision was a Republican issue at the last election, which no doubt had an important bearing upon Republican success, Congress, which is strictly Republican, is duty-bound to revise the tariff, down and not up. On the other hand, it must have in view the receiving of adequate revenue for governmental expenses. Should such revision downward be made in a manner to satisfy a large number of our people and fulfil the promise made by the Republican party, the cut in revenue would be such as would necessitate the enactment of income or inheritance taxes, which are offensive to many people. Further, if duties on certain articles are lowered too far there is danger of crippling industries which are now prosperous and em-

ploying American labor, which is always paid fifty, and sometimes a hundred per cent., more than foreign labor. Therefore, to give worthy industries necessary protection, and no more, to supply by duty ample revenue for government purposes and at the same time revise (downward) the tariff to fulfil the Republican promise, is not an easy matter.

As the chemical schedule was the first considered by the Ways and Means Committee, considerable notoriety was won in the daily press by those asking for duties on chemicals, to be made for the first time in the United States, and by those who had the temerity to petition for an increase in duty on chemicals now made in this country.

The United States must acknowledge Germany's superiority in chemical products, particularly the finer chemicals. The German government has fostered its chemical industry more than any of its other industries. She realizes more than any other nation that chemistry is the foundation of most of its industries and consequently aids it in all possible ways. By not giving proper protection to infant chemical industries, the United States government not only discourages the development of this particular industry, but to a certain degree retards the progress of many other industries which are founded on chemical reactions, or are users to a greater or less degree of chemical products.

In considering duties on chemicals our legislators should have this in mind, first, that those chemicals should be admitted free of duty which are made from minerals or other natural products which do not exist in the U. S. in exploitable amount, *e. g.*, nitrate of soda and potash. Second, that as soon as a chemical manufacturer gives assurance that he intends to enter into the manufacture of a certain chemical now on the free list, a tariff should be placed on that article sufficient to offset the extra cost of the chemical due to higher cost of labor in this country. This sort of protection is what is needed to develop the chemical industry. It does not mean necessarily an increase in the cost of that particular article to the consumer, but it does prevent the foreign trade combination from dumping its surplus goods in this market at a ridiculously low price for a time to kill the American competition.

There is evidence in the proposed tariff bill that this principle has at least occurred to our legislators, for oxalic acid under the Dingley tariff is on the free list; the importations for 1908 amounted to 8,800,000 lbs. In the last few years American manufacturers have succeeded in producing this chemical and should have some protection. The present bill takes oxalic acid from the free list and gives it one cent a pound duty. On the other hand, our Solons have inconsistently denied the petition made for a duty, equivalent to difference in labor cost, of those who with abundant raw material, benzol, stand ready to manufacture aniline oil and salts and free the American consumer of the foreign trade combination on those articles.

Phosphoric, benzoic, phthalic and carbolic acids, whose imports amount to over half a million dollars in value, all on the free list under the present and the proposed bill, should bear duty if satisfactory assurance is made that American manufacturers can produce them in considerable quantities. Acetic acid remains the same as in the old bill, while boracic acid is reduced from 5c. to 2c. per lb.; lactic acid is cut from 3c. to 2c.; gallic acid from 10c. to 8c.; tartaric acid from 7c. to 6c. In many instances the Senate bill increases the duty imposed by the House; this is noticeably so in the case of artificial sulphate of lime, bichromate of potash, or soda, orange mineral and red lead The House attempted to make a reduction in the duty on lead acetate, but the Senate would not assent, retaining the old schedules. The Senate is hardly consistent in totally removing the 25 per cent. *ad valorem* duty which sodium cyanide carried under the Dingley bill and leaving a 12.5 per cent. duty on potassium cyanide. The House bill calls for a 12.5 per cent. duty on both. The retention of $6.00 a ton on sulphur in both bills seems unnecessary in view of the fact that the Standard Oil Co. is producing it at such a low figure that it has completely shut out the Silician product. The potash salts are naturally still held on the free list. Through the efforts of the fertilizer manufacturers crying "free nitrogen for the farmer," ammonium sulphate was placed on the free list in the House bill, reduced from a duty of three-tenths cent per pound, but it was put back to two-tenths by the Senate Of the ammonium sulphate consumed in this country, 90 per cent. goes into fertilizers. The fertilizer contains on an average 1 per cent. NH_3; if the duty of $6.00 a ton on sulphate is removed, it means a possible reduction of 24 cents on a ton of fertilizer which costs the farmer $35. Will the fertilizer manufacturer or the farmer get this twenty-four cents?

Bicarbonate of soda is reduced one-eighth of a cent per lb. and soda ash one-eighth.

The House was inclined to encourage the aniline color manufacturers of this country by giving them 35 per cent. instead of a 30 per cent. duty, as in the Dingley tariff. This would not more than offset the extra labor cost and would be a just recognition of the splendid work that Schoellkopf and Heller & Merz Co. have done in starting this industry in this country. But the Senate cut it back to 30 per cent. in spite of statements from consumers of the colors favoring the increase. The House also consented to remove from the duty list certain products which are the color makers' raw materials, namely, sulpho acids, paranitraniline, dimethylaniline and others, but again the Senate said no.

What the final bill in its amended form will be one cannot predict. It has been intimated that the President may have something to say about it later.

ECONOMY IN THE USE OF OXYGEN FOR COMBUSTION CARBONS.

In the steel works laboratory of to-day the consumption of oxygen gives rise to a considerable item on the laboratory invoice. An idea suggested by Mr. A. G. McKenna, of our company, has led to the development of a system by which the volume of oxygen formerly used to make a single carbon determination is now utilized for from six to eight combustions.

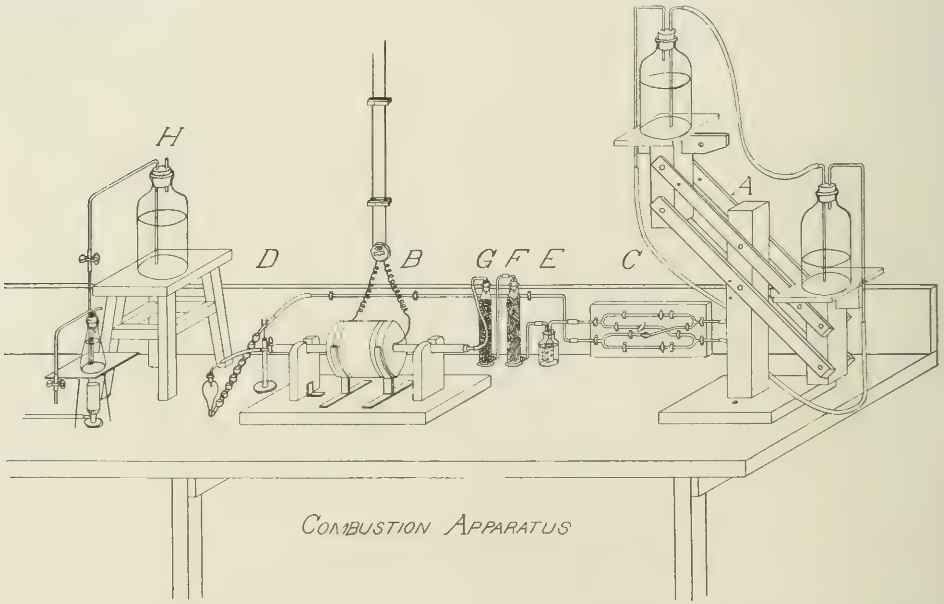
The method is shown in the accompanying illustration and consists simply of two eight-liter bottles on a balancing support, which when in one position causes the gas to flow by hydraulic pressure from one bottle through the system into the other; and, when in the other position, gives rise to an exchange in the opposite direction. This reverse of flow is sent through the combustion tube in the right direction by means of a small switchboard arrangement of four

glass stop-cocks so connected that they are operated in pairs and thus leave room for no confusion to the manipulator whenever he finds it necessary to reverse the current. From the bottles the gas passes through a purifying chain consisting of potash solution (1.27 sp. gr.), stick potash, and calcium chloride, and thence through the furnace, which is an ordinary tube of Imperial Berlin porcelain, wound with platinum foil and jacketed with alternate layers of magnesia pipe covering and intervals of air and heated by an electric current of such a strength as to give a constant temperature throughout the day of 1100° C. We have found this temperature to give the most satisfactory results in the direct burning of alloy steels. A small amount of coarse oxide of copper is kept in the tube just beyond the heated area to prevent the possible exit of any carbon monoxide from the tube.

The former method has been used very successfully by the author and easily gives checks within 0.004 per cent. of carbon, but as it is usually necessary to employ untrained labor in steel works laboratories, the latter method has been found to be more reliable in such hands in the long run.

The method in detail:

Weigh two grams of drillings (one gram in the case of furnace tests) into an ordinary platinum boat or filter plug, the former of which should be previously filled with quartz sand or ignited alumina, and the latter covered on the inside with a thin layer of freshly ignited asbestos. Fill the bulb tube with about 100 cc. of the warm barium hydrate solution and insert it in its proper place in the system. It is a good plan to syphon the solution from a large storage bottle into a 500 cc. Erlenmeyer flask, where it may be kept



COMBUSTION APPARATUS

The rest of the train may consist either of the usual purifying tubes and potash bulb as recommended by Blair, or simply of a Meyer bulb tube filled with a warm solution of barium hydrate (15 grams per liter). The barium carbonate which precipitates is filtered off, ignited and weighed as $BaCO_3$ containing 6.2 per cent. of carbon. This latter method gives consistent results which may easily be depended on for accuracy within two hundredths of one per cent. It is in common use in the region about Pittsburg and is sufficiently accurate for commercial purposes. It is possible, moreover, by this method to make quick tests for the melters in less than fifteen minutes, which is quite as rapid as, and far more satisfactory in the case of alloy steels than, the colorimetric method which is generally employed.

heated by an Argand burner turned low, and drawn off by a siphon into the bulb tube as needed. Push the platinum plug, or boat, into the hot part of the tube with a nickel rod and quickly put the stopper into the front end of the tube and turn on the two governing stop-cocks, allowing the gas to run at full speed until the white precipitate has just begun to form. Then leaving the return cock on full, turn the other one until the gas bubbles through at the rate of about two bubbles per second and continue the burning for eight minutes—in the case of furnace tests four minutes will suffice, especially if they are low in carbon, as is usually the case. Filter, using gentle suction, through a 11 cm. ashless filter supported by a small platinum cone, and wash with hot water. It is very convenient to have a four-liter flask kept full of hot water and elevated above the desk

near the filtering flask to allow it to be syphoned directly on to the filter, the flow of the stream being controlled by a small pinch-cock. If desired, the first filtrate may be reserved and later used in making up a fresh barium hydrate solution. When thoroughly washed, ignite in a crucible, and when cool brush into a counterpoised watch glass and weigh. This weight multiplied by three—less a correction of 0.01 per cent. found by a blank determination—gives the carbon in the sample. The factor in the case of furnace tests where only one gram is used is six.

In the sketch:

A. The tilting arrangement.
B. Electric furnace.
C. Keyboard for adjusting current of gas.
D. Meyer bulb tube.
E. Allihn gas washing bottle containing potash solution.
F. Calcium chloride cylinder containing stick potash.
G. Calcium chloride cylinder containing $CaCl_2$.
H. Barium hydrate solution.

WM. HERBERT KEEN.

LABORATORY OF
THE FIRTH-STERLING STEEL CO.,
WASHINGTON, D. C.

A SIMPLE COVER FOR ANALYTICAL WEIGHTS.

Probably every analyst is familiar with the annoyance occasioned by floating particles of dust and lint settling on the weights in a balance. The practice of always returning weights to the box has several disadvantages, and is usually considered unsatisfactory. An arrangement devised by the author to obviate this difficulty is in daily use in this laboratory, and may be of service elsewhere.

The base *B* has marked on it the shape, size, place and denomination of each weight. The exact size and shape of the base must, of course, be governed by the available space in the balance case, it being kept ordinarily in the space immediately in front of the pillar. The cover *C*, having a glass top with pasteboard sides high enough to clear the tallest weight, is somewhat smaller than the base, and rests on it when the balance is not in use, but is removed whenever the weights are needed. The use of glass in the cover makes it possible to place it over the weights without displacing any of them. This form of base greatly facilitates the reading of the weights, while the cover excludes dust at all times save when using them. As they are left at all times in the balance case, it is only necessary to remove the cover in order to have them in readiness for immediate use. The device may be obtained from Eimer & Amend.

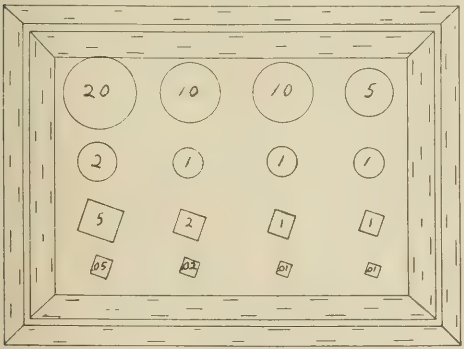


Fig. 1 (*B*).

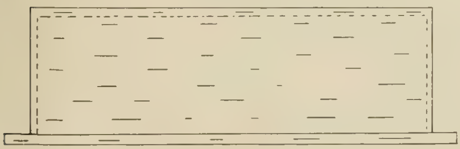


Fig. 2 (*C*).

L. T. BOWSER.

OHIO AGRICULTURAL EXPERIMENT STATION,
DEP'T OF CHEMISTRY,
WOOSTER, OHIO.

THE "SIZE-WEIGHT" PERCENTAGE.

APRIL 8, 1909.

MR. HARRISON EVERETT ASHLEY,
NEWELL, WEST VA.

Dear Sir:—I have your letter of March 29th regarding the "size-weight" per cent. mentioned in my article "Accuracy in Sampling Coal." On page 164 of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, it says: "The size-weight percentage ...... is the percentage of the largest pieces of slate to the total weight of the sample previous to its last division or quartering." If the largest pieces of slate weighed one pound and the sample to be divided weighed one hundred pounds, the "size-weight" per cent. would be one. If the sample had been crushed so that the largest pieces weighed only 0.1 lb. each the "size-weight" per cent. would be 0.1 per cent.

Unfortunately, in the reproduction of Fig. 2 the values of the "size-weight per cent. were omitted. The 4th, 8th, 12th and 16th heavy lines should be numbered 1, 2, 3, and 4, respectively.

Trusting this explanation clears up the matter, I am,

Yours very truly,

E. G. BAILEY.

DEFINITION OF "GASOLINE."

NEW YORK, April 13, 1909.

To the Editor of the Journal of Industrial and Engineering Chemistry:

DEAR SIR:—On page 261 of the *Journal* for April, 1909, under "Note on Turpentine," reference was made to "very light naphtha" and "exceedingly light petroleum products" as "not intended to include ordinary gasoline, but merely such unusual products as hexane, petroleum ether, etc."

Would it not be well to have the term "gasoline" or gasolene defined?

1. As to composition, whether composed of pentane, hexane, heptane, etc., and which hydrocarbon predominates.

2. Boiling-point limitations.

3. Whether or not, it is a part of the well-known "petroleum ether," or an entirely separate portion of "naphtha" distillate; and, the relations between it and the hydrocarbon fluid known as "benzine," whether inclusive or not.

Commercially, two or three grades of gasoline are known and the lightest might refer to petroleum ether. Some speak of the "benzines" as coming after the "gasolines."

According to Richter's "Organic Chemistry," the fractional distillation of American petroleum yields various products:

Petroleum Ether—B. p. 50°–60° C.; sp. gr. 0.665–0.67 (Pentane and Hexane).

Petroleum Benzine—B. p. 70°–90° C.; sp. gr. 0.68–0.72 (Hexane and Heptane).

Ligroin—B. p. 90°–120° C.; sp. gr. not given (Heptane and Octane).

Burning Petroleum—B. p. 150°–300° C.; sp. gr. 0.78–0.82 (Kerosene).

Where would "gasoline" come in under such a classification?

In Merck's 1907 Index, gasoline seems to have been omitted. Instead, "Benzine" is described as "Petroleum Ether; Naphtha; Petroleum Naphtha."

According to Thorp's "Outlines of Industrial Chemistry," 1899, p. 292, "The benzine distillate yields:

$$\left.\begin{array}{l}\text{Cymogene, b. p.} = 32^\circ\text{ F.; sp. gr.} = 0.590\text{–}0.610\\ \text{Rhigoline, b. p.} = 60^\circ\text{ F.; sp. gr.} = 0.625\text{–}0.631\\ \text{Gasoline, b. p.} = 115^\circ\text{ F.; sp. gr.} = 0.635\text{–}0.666\end{array}\right\}\text{Petroleum ether}$$

C Naphtha (Benzine), b. p. 122°–140° F.; sp. gr. 0.678–0.700, etc., etc."

Judging from this, gasoline would be one of the ingredients of petroleum ether, and "Benzine" a separate commodity.

Gill, in his "Oil Analysis," under Petroleum Products, mentions the "Naphtha Distillate" which is fractioned into four parts. The first, or "Crude Gasoline," is redistilled, giving:

Cymogene, b. p. 32° F. Largely butane for ice machines.

Rhigoline, b. p. 65° F. Largely pentane for local anaesthesia.

Petroleum Ether, "Sherwood Oil," "Gasoline," b. p. 100°–150° F. Largely hexane for gas machines and fat extractions.

Gasoline, Canadol, b. p. 150°–190° F. For large oil extraction.

In this case, petroleum ether is "gasoline" and does not include cymogene nor rhigolene, as in Thorp's classification. Again, canadol is apparently gasolene but not petroleum ether, although, according to Merck's 1907 Index, canadol is "Very Light Petroleum Ether."

Stillman's "Engineering Chemistry," 1897, p. 364, gives the following:

1. Naphtha group comprises:

Cymogene, a gas, boiling-point 0° C., specific gravity 110° B.

Rhigolene, liquid, boiling-point 18.3° C., specific gravity 100° B.

Petroleum ether, boiling-point 40° to 70° C., specific gravity 85° to 80° B.

Gasolene, boiling-point 70° to 90° C., specific gravity 80° to 75° B.

Naphtha (Danforth oil), boiling-point 80° to 110° C., specific gravity 76° to 70° B.

Ligroine, boiling-point 80° to 120° C., specific gravity 67° to 62° B.

Benzene, boiling-point 120° to 150° C., specific gravity 62° to 57° B.

Notice the overlapping of the boiling-points for gasolene, naphtha, and ligroine; also, that gasolene has apparently the same boiling-point (70° to 90° C.) given for "Petroleum Benzine" in Richter's "Organic Chemistry."

It might be interesting to know the distinction between petroleum ether and the gasoline used for automobiles, and whether the latter is a variable mixture of hydrocarbons.

Very respectfully yours,

FREDERIC S. HYDE.

CONTROLLING THE CONSISTENCY OF BITUMINOUS BINDERS.[1]

In the asphalt paving industry it was early recognized that some means of measuring the consistency of the asphaltic cement in use was absolutely essential if uniform results were to be achieved, and H. C. Bowen invented a penetration machine in 1888 for this purpose. The asphaltic cement generally employed in sheet asphalt pavements is semi-solid, and must be heated to about 300° F. or more before it can be satisfactorily incorporated with hot sand in a power mixer. A penetration machine is now invariably employed in connection with all such work of importance.

This instrument consists of a weighted needle and a graduated scale upon which the movement of the former, in millimeters, can be measured. The standard conditions for the test are a No. 2 cambric needle under a 100-gram load, which is allowed to penetrate the sample of bitumen under examination for five seconds at 77° F. The New York Testing Laboratory penetrometer and Dow instrument are the two in general use, and operate upon the same principle (see *Proceedings* Am. Soc. Testing Materials, Vol. 7, p. 626).

In the present movement for good roads that will withstand motor-car traffic, a new and urgent demand has arisen for a form of bituminous binder to hold the road metal of macadam type of roads in place. The various bituminous substances which have been placed upon the market for such use have varied in consistency from that of water to a semi-solid substance. A great deal of experimental work has been done with various proprietary preparations, crude tars and oils, and engineers are rapidly gaining the experience which will enable them to prescribe the necessary physical characteristics of the material desired for each particular type of construction, rather than to depend upon the venders of such articles.

The consistency or fluidity of bituminous binders is of great importance, both as a first consideration to insure selection of the appropriate type, and, during use, uniformity and perfect control of the work, just as it is in the sheet asphalt paving industry. It is obvious that a binder intended for use as a surface dressing should be of quite a different consistency from one which is to be incorporated with stone to form the wearing body of the highway. No single preparation will answer all requirements.

It has been proposed that a temperature of 90° F. be considered as a normal standard at which to test the consistency of road binders of a bituminous nature, because that is a fair condition upon a road during suitable working weather, and a compound should be capable of being worked to some extent, at least, at this temperature, if it is to be mixed with cool stone or swept into the interstices of a roadbed. A much more fluid material is required for

[1] Reprinted from the *Engineering Record*, May 1, 1909.

such use than in the older forms of bituminous pavements, the mixture for which is taken from a central plant in a hot condition, and the standard forms of penetrometers mentioned above are not available for regulating the consistency of the same.

TESTS OF THE CONSISTENCY OF BITUMINOUS BINDERS FOR HIGHWAYS.

Material.	N. Y. T. L. viscosimeter at 90° F. Min. Sec.	Engler viscosimeter —100 cc flow at— 77° F. Min. Sec.	130° F. Min. Sec.	250° F. Min. Sec.
Refined water gas tar.	0 20	Too stiff	9 46	0 50
Crude coal-tar.......	0 30	Too stiff	9 38	0 50
Tarvia.............	1 30	Too stiff	Too stiff	1 2
Tarina.............	0 16	17 10	3 18	0 34
Texas flux oil........	0 51	Too stiff	.. ..	1 32
Calif. flux oil........	3 40	Too stiff	Too stiff	4 14
Headley oil, No. 2....	0 35	Too stiff	Too stiff	1 30
Headley oil, No. 4....	2 53	Too stiff	Too stiff	1 30
Headley oil, No. 4....	6 56	Too stiff	Too stiff	8 42
Genasco compound...	10 54	Too stiff	Too stiff	8 30
Genasco compound...	*69 55	Too stiff	Too stiff	Too stiff
Genasco compound...	11 54	Too stiff	Too stiff	9 28
Standard Oil Co.....	0 6	5 38	1 36	0 32
Standard Oil Co.....	0 12	Too stiff	3 0	0 38
Standard Oil Co.....	0 23	Too stiff	Too stiff	0 56
Standard Oil Co.....	0 39	Too stiff	Too stiff	1 18
Standard Oil Co.....	1 24	Too stiff	Too stiff	2 26

The Engler viscosimeter is in general use for testing fluid compounds, such as oils, at any desired temperature, but is not available for the highly cementitious and semi-fluid asphaltic materials now preferred by road engineers, except at temperatures above 200° F.

To provide an instrument for controlling the consistency of semi-fluid compounds intended for road building the author has elaborated a simple form of viscosimeter, originally suggested by Mr. E. C. Wallace, now with the Warren Brothers Company, which fills the gap for substances between those which are sufficiently fluid for the Engler type of viscosimeter and the semi-solid cements heretofore regulated by penetration instruments.

The apparatus, which is made by Howard & Morse, Brooklyn, N. Y., consists of two parts, an aluminum float or saucer and a conical brass collar. The two parts are shown in the drawing, and are made separately for reasons of economy, so that one or two of the floats will be sufficient for an indefinite number of brass collars.

In using the apparatus the brass collar is placed upon a brass plate, the surface of which has been amalgamated, and filled with the bitumen under examination, after it has been softened sufficiently to flow freely by gentle heating. The collar must be level-full, and as soon as the bitumen has cooled sufficiently to handle it is placed in ice water at 41° F. for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at 90° F., or any other temperature desired.

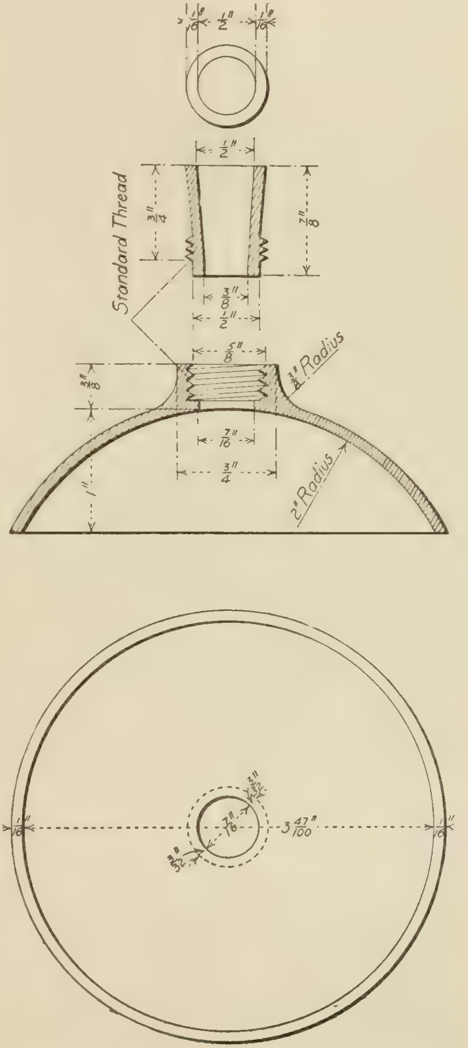
As the plug of bitumen in the brass collar becomes warm and fluid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface of the same.

The time, in seconds, elapsing between placing the apparatus on the water and when it sinks is determined most conveniently by means of a stop-watch, and is considered as the consistency of the bitumen under examination.

[1] N. Y. T. Laby. test at 150° F. = 2 min. 18 sec.

This device has been in general use in the New York Testing Laboratory for some time. An equipment of 12 brass collars, 2 aluminum saucers, a nursery refrigerator for ice water, and an open tank holding about one quart of water and heated by a Bunsen burner is sufficient for testing a great many samples. A thermostat in the water bath will assist in maintaining a constant temperature.

From the data presented in the above table, it will



Instrument for determining the consistency of road binders.

be observed that this device is available at 90° F. for testing almost any compound used in road building except light oils.

In conclusion we should perhaps explain that we appreciate the fact that this device and the proposed method for its manipulation may be open to serious criticism as a strictly scientific method of determining viscosity. It is, therefore, not presented as such, but as a practical tool for meeting an emergency which is urgent and now confronting all road engineers.

The Engler viscosimeter for tests at 250°–350° F. and the New York Testing Laboratory device at 90° F. provide satisfactory means for fixing the two ends of bituminous road compounds.

C. N. Forrest.

BOOK REVIEWS AND NOTICES.

Handboek ten Dienste van de Suikerriet-Cultur en de Rietsuiker-Fabricage of Java. Edited by the United Sugar Experiment Station of Java. 3 volumes. Amsterdam: J. H. de Bussy.

These 3 volumes, which are the first of a series of works by different experts upon the sugar cane industry in Java, constitute the most complete treatise which has yet appeared upon the sugar cane. While the books are written entirely from the standpoint of Java conditions, the subject matter is of such general applicability that this series of books will be found invaluable to all readers of Dutch who are interested in the cultivation of sugar cane and its manufacture into sugar.

Vol. I. **Methoden van Onderzoek der de Java Rietsuiker-Industrie Voorkomende Producten, Afvalproducten, Brandstoffen, Meststoffen, Chemicalien, Water, Smeerolien, Enz.** By H. A. P. M. Tervooren, Assistent aan het Proefstation voor Suikerriet in West-Java, "Kogok." 2nd. Edit. 1907. 367 pages, 46 cuts. Price, bound, f 7.50.

The second edition of this well known work is an expansion along the general lines of the first edition. Exact descriptions are given of methods for polarization and analysis of sugar cane products as cane, bagasse, juice, syrup, massecuite, sugar, molasses, etc., as well as of methods for the examination of all materials relating to cultivation and manufacture, such as fertilizers, lime, water, fuel, flue-gases, hydrosulphite, ultramarine, lubricating oils, molascuite, sulphur, etc. The last 40 pages of the book are devoted to laboratory reagents, preparation of standard solutions, use of indicators, etc. The 8 page list of apparatus and chemicals necessary for a sugar control laboratory will be found of special value to those contemplating such an installation.

The book is well arranged and completely up to date. The 13 pages, for example, devoted to the refractometer and its use in the sugar-house, represent the first attempt to condense into practical form the copious literature which has recently appeared upon this subject.

Vol. II. **De dierlijke Vijanden van het Suikerriet en hunne Parasieten.** By W. van Deventer, Assistent aan het Proefstation voor Suikerriet in West-Java "Kagok." 1906. 298 pages, 71 cuts, 42 colored plates. Price, bound, f 15.

This treatise upon the animal foes and parasites of the sugar cane is a compilation of the exhaustive researches published in past years by Zehntner, Krüger, and Kobus, together with much new material contributed by the author. It need hardly be stated that the greater part of the work (272 pages) is devoted to the insect enemies of the cane, which are especially prevalent and noxious in Java. The general distribution of the insects described may be seen from the following summary:

Coleoptera (beetles, etc.), 6 families, 19 species.
Lepidoptera (moths, etc.), 8 families, 34 species.
Diptera (flies, etc.), 2 families, 2 species.
Rhynchota (plant-lice), 5 families, 22 species.
Orthoptera (grasshoppers, etc.), 6 families, 29 species.

The remainder of the book is given to a description of a miscellaneous lot of enemies of the cane—apes, rats, mice, wild hogs, birds, crabs, nematodes, etc., of which some 20 different species are described.

The volume is not only an important one from the biological standpoint, but its very full directions for combatting the attacks of the various animal foes and parasites of the cane give the book great practical value to the planter.

The photographic reproductions and colored plates of the volume are splendidly executed and form a most valuable adjunct to the descriptive matter of the text.

Vol. III. **De Fabricatie van Suiker uit Suikerriet op Java.** By H. C. Prinsen Geerligs, Directeur van het Proefstation "Kagok" te Pekalongan. 1907. 449 pages. Price, bound, f. 7.50.

The author of the third volume of this series, whose name is almost synonymous with that of the Java Sugar Industry, needs no introduction to the Sugar World. The present work is an amplification of his previous book, published in 1902, upon "Cane Sugar and the Process of Its Manufacture in Java," which obtained such a wide success.

In his preface Mr. Geerligs states that he has endeavored to condense the results of all chemical researches relating to the constitution of the sugar cane and to the manufacture of sugar therefrom. With this end in view he has avoided so far as possible all discussion of sugar house machinery and equipment, and this more especially since the latter will form the subject matter of Vol. IV in the series of the Handboek.

In the first part of the volume (82 pages) the author discusses the chemical properties of the different constituents of the sugar cane—sucrose, dextrose, levulose, starch, cellulose, pentosans, pectin, acids, wax, nitrogenous substances, mineral matter, etc.—and the distribution of these in the different tissues of the cane.

In the second and principal part of the volume (306 pages) the manufacture of sugar from the cane is taken up. The subject matter of this division is indicated in the following summary:

1. *Extraction.*—Milling, diffusion, composition of juice, composition and fuel value of bagasse, etc.

2. *Clarification.*—Defecation and its influence on the juice constituents. Carbonatation and its influence on the juice constituents. Lime and liming, sulphurous acid, hydrosulphites, phosphoric acid, electrolytic methods, etc. Filtration.

3. *Evaporation.*

4. *Curing.*—Crystallization in motion, purging, working-up of after-products, composition of sugar, conservation of sugar during transport and storage.

5. *Molasses.*—Definition and theory of formation, composition of Java molasses, working up of molasses, etc.

In the third part of the volume (61 pages) the author takes up methods of factory control, calculation of extraction, determination of yields and losses, etc. Specimen pages of forms for factory work are given, together with the tabulation of results obtained in 96 Javan sugar houses.

The whole book is typical of Mr. Geerligs' characteristic breadth of treatment and in his compilations he has given not only the results of his own numerous investigations published in the Archief voor de Java Suikerindustrie, but he has also included the researches of investigators in Louisiana, Hawaii, and other cane-producing countries. The completion of this book, coincident with the author's retirement from the directorship of the Sugar Experiment Station Kagok, represents the crowning achievement of 20 years' activity in the Java sugar industry.

Those who are unable to read Dutch will be glad to know that Mr. Geerligs' volume of the Handboek is soon to be printed in English. It was the reviewer's privilege recently to go over a part of the proof of this translation with Mr. Geerligs in person. While it has been deemed advisable to omit the more local part of the Dutch volume relating to methods of factory control in the translation, the two more general parts upon the composition of the cane and the manufacture of sugar therefrom will be found to be even more complete than the Dutch original.

Mr. Geerligs' many friends in all parts of the world will wish him continued and greater successes at home in the continuation of his work in the service of his country and of the sugar industry. C. A. Browne.

Die Raffination des Zuckers. By Wilhelm Gredinger. Vienna and Leipzig: A. Hartleben. 283 pages with 125 cuts. Price, 12 Marks, bound.

This work, to quote from the author's preface, was written not simply as a book of reference for the practical sugar maker, but also as a guide and handbook for the student.

Owing perhaps to the disinclination of practical sugar men to communicate the knowledge gained by experience, a complete comprehensive work upon sugar refining has up to the present time not yet been written. It was hoped from the preliminary announcement of the publishers that the present work of Gredinger's would fulfil this long-felt need; this expectation, however, has not been fully realized. In the first place the author has limited his treatment of the subject almost exclusively to Austrian conditions with the result that comparatively little is said of the processes of refining followed in other countries. Over 50 pages of the book are devoted for example to the manufacture of cube sugar while that of granulated and other forms of sugar made elsewhere is dismissed with scanty mention. In the second place the language of the author is so full of localisms, unusual expressions of non-Germanic origin (usuelle, praedisposition, etc.) and unfamiliar idioms that the reader is often unable to grasp the writer's meaning. The criticisms of the book by von Lippmann and other German reviewers are particularly severe as to literary short-comings.

But aside from the two objections just named the present book by Gredinger will be found to contain much matter of interest. The sections upon affining and bone-black are especially well treated. The chapters on working-up of after-products and molasses are also comprehensive. The various methods of refining without the use of bone-black are briefly described and the questions of refinery losses and yields discussed. The strongest feature of the book is unquestionably the description of machinery and apparatus and the many valuable points of practical value which the author gives concerning refinery management are plainly the result of years of personal experience.

The book is printed upon good paper in plain Roman type and the illustrations and diagrams are for the most part clear and distinct. C. A. Browne.

Sugar, A Handbook for Planters and Refiners. By the late John A. R. Newlands and Benj. E. R. Newlands. London: E. & F. N. Spon. New York: Spon & Chamberlain. 856 pages, 236 figures, and 12 plates. Price, $10.00, bound.

Every student of sugar and sugar-making is familiar with the work "Sugar" by Lock and Newlands Bros., published in 1888 and now for a long time out of print. The old book in spite of the obsolete character of much of its material had obtained a wide popularity; it was broader than a limited treatise and for a general account of all that pertained to the agriculture and technology of sugar there was no other work with which it could be compared.

In his preface to the new edition the author states that he has endeavored to bring "the subject matter closely up to date." "By leaving out certain parts of the last edition of the book relating to matter which has become more or less obsolete, it has been found possible to introduce a very large amount of new material of a useful character without extending the size of the volume."

The great criticism of the previous edition was that so much of its information was out of date; it was hoped that the new book might be freed from these old encumbrances, and with the injection of new material fulfil the promises of the author and be brought "closely up to date." In the realization of this hope, however, the reader will be more or less disappointed.

Of the 856 pages in the new edition 580 are reprinted without change from the old book. Where methods and processes have remained unaltered the incorporation of material from a previous edition is perfectly justifiable, but in the present case this has been followed with too much literalness, as in the chapter upon Melon Sugar which begins as 20 years ago "The preparation of syrup from the melon (Cucumis melo) is fast assuming some importance in America," and so on word for word to the end. The chapters upon Palm Sugar (18 pages), Sorghum Sugar (reduced from 32 to 7 pages) and Maple Sugar (11 pages, 1 page new) stand practically as they did before and leave the reader but little wiser as to the industrial and economic changes which have taken place in these fields of sugar-making. The chapters upon Beet Molasses (13 pages) and Starch Sugar (46 pages) are reproduced without alteration, notwithstanding the many improvements in these departments during the past quarter-century.

Of the 270 pages of new material added to the present edition the 72 pages upon Production and Commerce have

been entirely rewritten; there have also been added 52 pages to the very full chapter on Cane Sugar Factories, 45 pages to the two chapters upon Extraction and Defecation of Beet Juices, 30 pages to Refining and 21 pages to Rum and Alcoholic Liquors These additions are well written and the text is enriched with many new diagrams and illustrations.

The author in his readjustment of material has unfortunately limited his pruning and grafting almost exclusively to the mechanics and has neglected the chemistry of sugar-making. The excellent bibliography of sugar literature mentioned in the introduction shows that he had the very latest researches at hand upon the chemistry of the sugar cane and sugar beet; it is difficult to understand, therefore, why the author should have reprinted for example the antiquated results of Stenhouse and of Icery (1865) instead of quoting the more recent and far more reliable work of Geerligs. The nomenclature of chemical terms is also in many places archaic and misleading, as for example the continued use of the terms crystallizable sugar for sucrose and uncrystallizable sugar for reducing sugars, globular and granular matter of cane juice, etc. Faulty discrimination is shown in the choice of references as for example (p. 107): "The uncrystallizable sugar present in juice from sound canes consists according to Winter, entirely of dextrose, levulose being found only in diseased and altered canes." The insertion of such matter is doubly unfortunate for it not only misleads the student beginner, but serves to disqualify the book completely in the eyes of the better informed.

Notwithstanding the great progress made in sugar analysis the chapter upon methods is reproduced with but very few additions from the old book. Faulty and obsolete methods of analysis are prescribed and no references at all made to the more recent methods of procedure such as those adopted by the international commission or such well known processes as that of Herzfeld for determining reducing sugars.

The volume, however, as indicated by the title is a handbook for planters and refiners and not a treatise for chemists. For descriptions of agricultural methods and processes of manufacture the reader will not be disappointed; these are all very complete and easily comprehended by means of the numerous plates and illustrations. Much of the material contained in this as in the previous edition is unique in character and for many facts of interest the reader would search elsewhere in vain.

The typography of the volume is good and the illustrations for the most part distinct. In a few cases, however, the cuts (as on page 351) have been reduced to such an extent that there is lack of detail. The binding-in of 32 pages of advertising matter is going somewhat beyond the limit in such matters and in a book already over-weighty only adds to the cumbersomeness of the volume. C. A. Browne.

Laboratory Manual of Dyeing and Textile Chemistry. By J. Merritt Matthews, Ph.D. New York: John Wiley & Sons. 363 pp. Price, $3.50.

This book is intended as an elementary laboratory manual or guide for students in the textile schools, and in other institutions where the many branches of technical chemistry are taught. To more clearly illustrate the points in question the experimental method has been adopted, and is supplemented by additional notes and quiz questions which serve more firmly to fix the information gained by the experiment.

The subject matter is divided into twenty eight sections, each section corresponding to a weekly apportionment of study. The experimental part will require from eight to twelve hours of laboratory practice each week, though sufficient experiments have been given to allow the teacher considerable latitude as far as selection of material and length of laboratory practice are concerned.

The book starts out with a study of the fibers, and shows the action of acids, alkalies, and salts upon cotton and wool. Next comes a study of the methods employed for scouring of wool, cotton, and silk, followed by the bleaching operations. Thus the various sections follow each other in natural sequence, leading by degrees through the simpler to the more involved processes of dyeing and analytical tests.

In section five is found a classification of the dyes, followed by several sections upon their application and testing, together with a complete list of all the dyestuffs on the market. This last feature is a novel one and is to be highly commended. The sulphur colors are assigned quite an important position, while the sections on mordant dyes, developed dyes, vat dyes, and natural dyes are very ably treated. Considerable space is devoted to the testing of dyes, and the analysis of textile fabrics, while the appendix contains much valuable data for the dyer and textile chemist.

The advent of this book is the fulfilment of a long-felt want for a text on dyeing and textile chemistry. The method of presentation is clear and concise, and as care has been taken to avoid too scientific explanations, it becomes all the more valuable for the purpose for which it is designed. The subject treated is a technical one, and an endeavor has been made to present it in a technical manner; that is to say, definite facts have been presented in a definite form. The book as a whole is well written, and the author deserves great credit for the manner in which he has handled the subject. Allen Rogers.

Die Theorie der Färbevorgäuge. By Dr. Procopios Zacharias, Privatdozent au der Universität Athen. pp. viii+420. Berlin: Verlag für Textil-Industrie. 1908.

This volume forms an interesting addition to the subject of textile chemistry. It is in reality a German edition, greatly enlarged, of Dr. Zacharias' previous work in Greek. On this account it is especially acceptable, as the latter book (by reason of the language in which it was written) was available to but a limited class of readers.

Though Dr. Zacharias, himself, has done considerable research in the subject of the "Theory of the Dyeing Process," and has embodied his results and theories in his book, nevertheless the chief value of the present volume is its collection of work done by all previous chemists in this field. This compilation is both historical and critical, and extends from the work done by Hellot in 1734 up to and including all work of the present time relative to the subject. Especial attention is paid to the experimental work of Chevreul, Persoz, Bolley, E. J. Mills, Mueller-Jacobs, Knecht, Vignon, Weber, Georgievics, Guehm and Rötheli, Hallitt, and F. Krafft, and a critical discussion is carried on concerning the various theories of dyeing as advanced by these chemists.

The ideas of Dr. Zacharias, himself, have a mathematical

bias with a tendency to reduce the process of dyeing to a differential equation. Though this makes an attractive proposition for the physical chemist, it is not much of an aid to either the practical dyer or the textile chemist.

This book will hardly be of much value to the technical chemist or dyer, but to the broader mind interested in the physical chemistry of textile processes it will prove an interesting and instructive volume. Though the author has not given us much original matter, yet he has assiduously collected a large mass of material relative to dyeing and arranged it in an intelligent and more or less systematic manner. The lack of an index is a serious drawback to the value of the book. J. MERRITT MATTHEWS.

Bedeutung der Kolloide für die Technik. PROF. KURT ARNDT. 40 pp. Dresden: Steinkopff. Price, 1 Mark.

This brochure is a simply and clearly written treatise on recent colloid work connected with a number of technical fields. It is quite full of suggestive matter which must interest chemists working along the lines touched upon. The treatment of each subject is altogether too brief to satisfy more than the general reader. After a brief description of colloids and their characteristics, the application of colloidal chemistry to the following subjects is considered: Ruby and opal glasses, gold and silver mirrors, tungsten lamp filaments, ceramics, cements and glues, color lakes, dyeing, tanning, soaps and fats, sewage purification, and soil fertilization. W. R. WHITNEY.

Post's Chemisch-technische Analyse. Handbuch der analytischen Untersuchungen. Herausgegeben von DR. BERNHARD NEUMANN. Zweiter Band. Braunschweig: F. Vieweg und Sohn. 1909. 800 pp., xiv, 1515, 252 illustrations. Ladenpreis, M. 37.50.

This is the second and final volume of the new edition of an important publication covering Kalk, Kalksteine, Zement und Gips by Drs. Segers und Cramer, pp. 1–80; Touwaren by the same, pp. 81–172; Glas und Glasuren, by the same, pp. 173–208; Rubenzucker, by Dr. R. Frühling, pp. 209–352; Stärke, Dextrin, Traubenzucker, by Dr. E. Parow, pp. 353–424; Bier by Drs. H. Vogel and C. Bleisch, pp. 425–470; Wein, by Dr. P. Kulisch, pp. 471–560; Spiritus und Presshefe, by Dr. H. Hanow, pp. 561–626; Essig, Essigsäure, Verbindunges der Essigsäure, Holzgeist, by Dr. F. Rothenbach, pp. 627–658; Handelsdünger, Stallmist, by Dr. Paul Wagner, pp. 659–680; Bodenarten und Emtesubstanzen, by the same, pp. 681–688; Die Luft, by H. Chr. Nussbaum, pp. 689–716; Atherische Öle, by Dr. J. Helle, pp. 717–792; Leder und Gerbstoffe, by Dr. Max Philip, pp. 783–850; Leim, by Dr. Richard Kissling, pp. 851–860. Tabak, by the same, pp. 861–870; Kautschuk und Kautschukwaren, 871–908; Spring und Zündstoffe, by Dr. H. Kash, pp. 909–1048; Der Steinkohlentur, by Dr. G. Schultz, pp. 1049–1084; Farbstoffe und Zugehörige Industrie, by the same, pp. 1085–1487; Sachregister, 1490–1514. What was said of Volume I in a previous notice applies also to Volume II. EDWARD HART.

Sprechsaal Kalender for the Ceramic, Glass and Allied Industries. J. KOERNER. 115 pp. Coburg: Mueller and Schmidt.

This publication of 115 pages is one of the most unique attempts in chemical technology. It summarizes all of the recent work done in Germany in the field of silicates, paying particular attention to the accurate, scientific researches such as the work of Berdel on the vitrification of clay substance, quartz and feldspar, insoluble glazes, testing of glass, Rieke's researches on mica, lime, magnesia and titanic acid, Simonis' results on mixtures of kaolin, quartz and feldspar, etc. In addition a good deal of general information is given regarding bodies, glazes and glass which is very useful. Dr. Koerner is to be congratulated in producing such a radical change in the makeup of such a publication, and it is to be hoped that this feature will be maintained in the future and include also the results of American research along these lines. A. V. BLEININGER.

The Testing and the Properties of Sand Lime Bricks. H. BURCHARTZ. Royal Materials Testing Station, Gross Lichterfelde. 105 pp. Berlin: Julius Springer.

Exhaustive tests and statistics on the properties of these bricks. This work is probably the most thorough ever done in this field. The recommendations for specifications governing the purchase of sand-lime bricks are especially interesting and are as follows: The bricks must possess good structure and must have a good ring. The water absorption should not be more than 15 per cent. of the weight of the dry brick. When used as backing up bricks or as facing they should have a crushing strength of not less than 2100 pounds per sq. in.; the regular run of hard brick should show a crushing strength of not less than 2800 pounds per sq. in., tested in the dry condition. The bricks must not soften in water and the crushing strength when tested wet should not be lower than when tested dry by more than 15 per cent. They must resist twenty-five successive freezings. The loss in crushing strength on freezing should not be more than 20 per cent. as compared with the dry strength. The crushing strength to be accepted should be the average of ten tests. Variations amounting to 10 per cent. below the minimum requirement in strength are permissible. A. V. BLEININGER.

Bulletin No. 9, Illinois State Geological Survey, "Paving Brick and Paving Brick Clays of Illinois. By C. W. ROLFE, R. C. PURDY, A. N. TALBOT and I. O. BAKER. University of Illinois, Urbana. 1908.

This is a volume of 316 pages, containing three plates and thirty-three illustrations. It covers the Geology and Classification of Clays, 46 pages; Qualities of High-Grade Paving Brick and Tests Used in Determining Them, 87 pages; Qualities of Clays Suitable for Making Brick, 84 pages; Pyro-Physical and Chemical Properties of Paving Brick Clays, 60 pages; Clays Tested which Are Suitable for Use in the Manufacture of Paving Brick, 9 pages; Construction and Care of Brick Pavements. 16 pages. W. D. RICHARDSON.

The Spanish Translation of the Pharmacopoeia of the United States of America. Eighth Revision. American Druggist Publishing Co., New York. Price, cloth, $5.00.

The close and friendly relations existing between the United States and Spanish-speaking countries will be further cemented by the appearance of this book, which has been three years in actual preparation. Some delay has been experienced in the completion of the translation, due mainly to the passage of the United States Food and Drugs Act,

June 30, 1906, making necessary some additions and changes in the chemical tests and standards.

The Spanish translation is from the latest revised text and it is confidently hoped that it may prove a potent factor in elevating the professions of medicine and pharmacy by furnishing a guide to the preparation of medicines accurately from drugs of the highest quality.

The Committee of Revision and the editor of the Spanish edition have labored earnestly to produce a standard work which will merit the approbation of scientific men, and science knows no language and no country.

JOSEPH P. REMINGTON,
Chairman of the Committee of Revision of the Pharmacopoeia of the United States of America (8th Rev.).

The Portland Cement Industry from a Financial Standpoint. E. C. ECKEL. *Moody's Magazine.* New York. Cloth; 6x9 ins. pp. 93; with two-page map of the United States, showing locations of Portland cement plants. Price, $2.00 net. C. N. WILEY.

NEW BOOKS.

Die Bedeutung der Kolloide für die Technik. By PROF. KURT ARNDT. Dresden: Verlag von Theodor Steinkopff. Preis, M. 1.

Reichenbach als Beobachter, S-A aus "Archiv für die Geschichte der Naturwissenschaften und der Technik." By A. BAUER. Leipzig: Verlag F. C. W. Vogel, 1909.

Tabellen für Berechnun von Kalianalysen. DR. R. EHRHARDT. Halle a/S: Wilhelm Knapp's Verlag. 1908. 8°, 69 pp. Price, M. 3.00 net.

Malmaterialienkunde als Grundlage der Maltechnic. By PROF. A. EIBNER. Berlin: Verlag von Julius Springer, 1909. Preis, geh., M.12; geb., M.13.60.

Cement Pipe and Tile; Advantages of Cement for Pipe and Tile, Methods of Manufacture, Tests, Costs, etc. By E. SMITH HANSON. Chicago: Cement Era Publishing Co., 1909. 110 pp., il., cl. Price, $1.00.

Verdampfen, Kondensieren und Kühlen. Erklärungen, Formeln und Tabellen für den praktischen Gebrauch. By E. HAUSBRAND. 36 fig., 74 tabellen, 4 Aufl. Berlin: Verlag Julius Springer, 199. Price, geb., M.10.

Untersuchung des Wassers an Ort und Stelle. By HARTWIG KLUT. Berlin: Verlag von J. Springer. Mit 29 figuren und 154 ss. Preis, M. 3.60.

Examination of Water for Sanitary and Technic Purposes by Chemical and Bacteriological Methods. By H. LEFFMAN. 6th ed., rev. and enl., 1909. Phila.: P. Blakiston's Son & Co. il., 12°. Price, $1.25.

Laboratory Manual of Dyeing and Textile Chemistry. By JAS. MERRITT MATTHEWS. New York: John Wiley and Sons, 1909. 12+363 pp., 8°, cl. Price, $3.50.

Farbenchemisches Praktikum zugleich Einführung in die Farbenchemie und Farbereitechnik. By RICH. MOHLAN and HANS TH. BUCHERER. Leipzig: Veit & Co. 7 Taf., 8°. Preis, M. 8.

Systematic Treatment of Metalliferous Waste. By L. PARRY. London: *The Mining Journal*, 1909. Price, 5s. net.

A Manual of Volumetric Analysis, for the Use of Pharmacists, Sanitary and Wood Chemists. By H. W. SCHIMPF. 5th ed., rewritten. New York: John Wiley & Sons, 1909. 745 pp., figs., 8°, cl. Price, $5.00.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN ELECTROCHEMICAL SOCIETY.

Very appropriately the Fifteenth General Meeting of the American Electrochemical Society was held at Niagara Falls, Canada, May 6, 7 and 8, 1909. Thus the society met for the third time at the great American center of the electrochemical industries. The headquarters for the meeting was the Clifton Hotel on the Canadian side and the sessions were held in the Convention Room of the Hotel. The total number of members and guests registered was 316. The principal drawing feature of the meeting was easily the symposium on the Electrometallurgy of Iron and Steel. Unfortunately a number of those scheduled on the program to read papers were not present and their papers were read by others. The program was as follows:

PROGRAM.

THURSDAY, MAY 6TH.

8.30 A.M.—Registration. Writing room of Clifton Hotel.

9.30 A.M.—Symposium on the Electrometallurgy of Iron and Steel.

(1) Robert Turnbull, Resident American Engineer for Dr. P. L. T. Héroult.

"The Héroult Electric Steel Furnace."

(2) Paul Girod, Director, "S. A. Electrometallurgique Procédés Girod," Ugine, Savoie, France.

(3) Dr. A. Kjellin, Electrometallurgical Engineer Metallurgiska Patent Aktiebolag, Stockholm, Sweden.

(4) Cav. Ernesto Stassano, Director, Forni Ellectrici Stassano, Turin, Italy.

(5) Remo Catani, Electrometallurgist of the "Société Elba," Portoferraio, Elba, Italy.

"Large Electric Steel Furnaces in the Iron and Steel Industry."

(6) Ch. A. Keller, General Manager "Société des Etablissements Keller-Leleux," Livet, Isère, France.

"A Contribution to the Study of Electric Furnaces for the Electrothermic Treatment of Iron and Steel."

(7) Gustav Gin, Electrometallurgist "Société Procédés Gin," Paris.

(8) Henry D. Hibbard, Consulting Engineer, Plainfield, N. J.

"The Present Value of Electric Steel."

(9) F. A. J. FitzGerald, Consulting Electrometallurgist, FitzGerald and Bennie, Niagara Falls.

"The Application of the Lash Process to the Electric Furnace."

(10) P. McC. Bennie, Consulting Metallurgist, Niagara Falls.

"Electric Furnace Pig Iron in California."

(11) Jos. W. Richards, Professor of Metallurgy, Lehigh University.

"The Electric Furnace Reduction of Iron Ore."

1.30 P.M.—Intermission for Luncheon.

2.45 P.M.—Continuation of Discussion on the Electrometallurgy of Iron and Steel. Reading of papers left over from morning session.

(12) Furnace Electrode Losses. C. A. Hansen.

(13) The Working Limit in Electrical Furnaces Due to the "Pinch" Phenomenon. Carl Hering.

(14) A New Type of Ammeter for the Accurate Measurement of Alternating Currents above 1000 Amperes. E. F. Northrup.

(15) A New Radiation Pyrometer. Chas. E. Foster.

(16) The Automatic Registration of Temperatures. E. F. Northrup.

8.00 P.M.—Presidential Address, by the retiring President, Mr. E. G. Acheson. Subject: "The Electro-chemist and the Conservation of our National Resources."

9.00 P.M.—Smoker.

FRIDAY, MAY 7TH.

9.30 A.M.—Meeting of the Board of Directors. Clifton Hotel.

10.30 A.M.—Business Meeting of Society. Announcement of Election of Officers. Reading and Discussion of Papers.

(17) Addition Agents in Electrolytic Plating Baths. E. F. Kern.

(18) Electrolytic Precipitation of Lead and Zinc as Affected by the Addition of Certain Organic Compounds. S. A. Tucker and E. G. Thomsen

(19) Electro-deposition of Some Metals from Acetone Solution. H. E. Patten and W. R. Mott.

(20) The Deposition of Aluminium from Aqueous Solutions, using Rotating Cathodes. S. A. Tucker and E. G. Thomsen.

(21) The Electro-deposition of Platinum. W. J. McCaughey.

(22) Electrolytic Production of White Lead and Colors. John A. Yunck.

(23) The Electromotive Force of Cadmium Amalgams. G. A. Hulett.

(24) Thermodynamics of the Weston Standard Cell. G. A. Hulett.

(25) The Electrolytic Reduction of Nitric Acid—II. H. E. Patten and W. J. McCaughey.

1.30 P.M.—Adjournment for Luncheon.

3.00 P.M.—Take special cars to the Gate House of the Ontario Power Co. Walk to the plant of the Electrical Development Co., Ltd.; walk to the Canadian Niagara Power Co., thence to entrance of the Ontario Power Company, from which point elevator will take visitors to Power House in the Gorge and to the Transformer Station at the top of the bluff.

7.30 P.M.—Banquet. Clifton Hotel.

SATURDAY, MAY 8TH.

9.00 A.M.—Reading and Discussion of Papers.

(26) The Probable Electrical Nature of Chemical Energy. A. H. Patterson.

(27) Bakelite and Its Electrical and Electrochemical Applications. L. H. Baekeland.

(28) A Graphite Cathode Dish. J. W. Turrentine.

(29) Relative Efficiency of the Arc and Resistance Furnace for the Manufacture of Calcium Carbide. S. A. Tucker, W. A. Alexander and H. K. Hudson.

(30) Some Physical Properties of Silicon. C. I. Zimmerman.

(31) Magnetic Tests of Some Iron Alloys. C. F. Burgess.

(32) Further Experiments with Calcium Alloys as Reducing Agents. O. P. Watts and E. R. Suhm.

(33) Electrochemical Methods of Soil Analysis. F. K. Cameron.

(34) A Modified Oxy-hydrogen Gas Coulometer. J. W. Turrentine.

(35) Rapid Electrochemical Analysis—a Comparison of Several Methods. L. S. Palmer and R. C. Palmer.

(36) An Answer to Prof. Ganz's Questions on the Corrosion of Iron. W. H. Walker.

N. B.—Papers (31) and (36) will be called up on Thursday, if time permits.

1.30 P.M.—Adjournment for Luncheon.

2.30 P.M.—Take special cars at Clifton Hotel to plant of Development and Funding Co. (note under announcement of excursions, special conditions under which this invitation is extended to persons in allied lines of manufacture); thence take cars to plant of International Acheson Graphite Co.; thence to Power House of the Niagara Falls Power Company. Thence take cars to Main Street and walk to the Power House of the Niagara Falls Hydraulic Power and Manufacturing Company.

8.30 P.M.—The Niagara Club will tender the Society and its guests an "Open House" at the Club House, corner of Buffalo Ave. and First Street, Niagara Falls, N. Y.

AMERICAN SOCIETY FOR TESTING MATERIALS.

The Twelfth Annual Meeting of the Society will be held at the Hotel Traymore, Atlantic City, N. J., on Tuesday to Saturday, inclusive, June 29–July 3, 1909.

To avoid the unsatisfactory acoustics in the pavilion used last year for meeting purposes, and in order to be independent of elevator service, the sessions will be held this year in the first-floor parlors of the Hotel Traymore. The program will be arranged with a view of avoiding parallel sessions, and it is expected that provision will be made for an informal dinner and a smoker.

The Fifth Congress of the International Association for Testing Materials will be held in Copenhagen, September 7-11, 1909. Attention is again called to the fact that any member of the Society may become a member of the International Association by forwarding a remittance of $1.50 to the Secretary of the American Society, and filling out an application blank for membership which will be furnished on request. Members of the International Association are entitled to free copies of all official papers presented at the Congress, including reports of referees and committees on technical subjects. These papers will be printed in German, French and English, and may be procured in any one of these languages.

The non-official papers to be presented at the Congress, consisting of scientific papers by individual members, can be obtained by members of the International Association at a moderate additional charge, which has not yet been fixed. These papers will be printed in their original language only,

followed by abridged summaries in two other languages. A list of the titles of these papers will be forwarded in due course by the Secretary of the American Society to the American members of the International Association.

That the remarkable growth of the Society has been well sustained since the last annual meeting is shown by the following statistics. The total membership reported at the last annual meeting was 1,015. Since then 162 applications for membership have been approved, 28 members have resigned, and there have been two losses by death—V. S. Allien, July 13, 1908, and Thomas Gray, February 12, 1909—making a net gain of 132, and a present membership of 1,147.

SUB-COMMITTEES OF GENERAL COMMITTEES ON STANDARD SPECIFICATIONS FOR COALS, AMERICAN SOCIETY FOR TESTING MATERIALS.

SUB-COMMITTEE NO. 1.

Coals for Steam Power Plants.

Goss, Prof. W. F. M., Chairman, University of Illinois, Urbana, Ill.

Stott, H. G., 600 West 59th St., New York, N. Y.

Kolsem, J. C., Indiana Coal Op. Ass'n, Terre Haute, Ind.

McGreath, A. S., 121 Market St., Harrisburg, Pa.

Scholz, Carl, C. R. I. & P. Ry., Old Colony Bldg., Chicago, Ill.

Barrus, Geo. H., 12 Pemberton Square, Boston, Mass.

Capp, J. A., General Electric Co., Schenectady, N. Y.

Gibbs, A. W., Penna. R. R., Altoona, Pa.

Clark, D. O., Union Pacific Coal Co., Omaha, Neb.

Taylor, Ed. H., Old Colony Bldg., Chicago, Ill.

Fleming, H. S., 1 Broadway, New York, N. Y.

Winder, Jno. H., Clinchfield Coal Corporation, Roanoke, Va.

Hume, A. P., Engineer of Tests, American Bridge Co., Pencoyd, Pa.

Garrison, O. L., Big Muddy Coal & Iron Co., Wainwright Bldg., St. Louis, Mo.

Woodwell, J. E., Terminal Bldg., Park Ave. and 41st St., New York, N. Y.

Randall, D. T., U. S. Geological Survey, Pittsburg, Pa.

SUB-COMMITTEE NO. 2.

Coals for Producer Gas.

Fernald, R. R., Chairman, Case School of Applied Science, Cleveland, Ohio.

Carney, F. D., Pennsylvania Steel Co., Steelton, Pa.

Jones, John H., Pittsburg–Buffalo Co., Pittsburg, Pa.

Parr, Prof. S. W., University of Illinois, Urbana, Ill.

Atkinson, John B., St. Bernard Mining Co., Earlington, Ky.

Dulaney, B. L., Black Mountain Coal Land Co., Bristol, Tenn.

Rice, Geo. S., U. S. Geological Survey, Pittsburg, Pa.

SUB-COMMITTEE NO. 3.

Domestic and Heating Coals.

Woodwell, J. E., Chairman, Terminal Building, New York, N. Y.

Lathrop, W. A., 108 South 4th St., Philadelphia, Pa.

Bemont, A., 2114 Fisher Bldg., Chicago, Ill.

Richards, W. J., P. & R. C. & X. Co., Pottsville, Pa.

Toulmin, Priestley, Lehigh Coal Mining Co., Birmingham, Ala.

Moldenke, Richard, Watchung, N. J.

Choney, E. H., 1712 Marquette Bldg., Chicago, Ill.

Dougherty, P. L., U. S. Treasury, Washington, D. C.

SUB-COMMITTEE NO. 4.

Metallurgical Coals (for Coke, Gas and Smithing Coals).

Robinson, C. S., Chairman, Youngstown Sheet & Tube Co., Youngstown, Ohio.

Blauvelt, W. H., Semet-Solvay Co., Syracuse, N. Y.

Eilers, Anton, Am. Smelt. & Ref. Co., 165 Broadway, New York, N. Y.

Moldenke, Richard, Watchung, N. J.

Schluederberg, G. W., Pittsburg Coal Co., Pittsburg, Pa.

Harris, J. R., Tenn. Coal, Iron & R. R. Co., Ensley, Ala.

Belden, A. W., U. S. Geological Survey, Pittsburg, Pa.

Howard, Chas. W., Gen. Mgr., New Etna Coal Co., Chattanooga, Tenn.

Hume, A. P., Engineer of Tests, American Bridge Co., Pencoyd, Pa.

Hahman, William, Lilly Coal Co., Masonic Temple, Altoona, Pa.

Murray, W. J., Victor Fuel Co., Denver, Colo.

Brady, Wm., Chief Chemist, Ill. Steel Co., S. Chicago, Ill.

SUB-COMMITTEE NO. 5.

Coals for Illuminating Gas (and Water Gas).

White, Prof. Alfred H., Chairman, University of Michigan, Ann Arbor, Mich.

Clark, Walton, Broad and Arch Sts., Philadelphia, Pa.

Jones, John H., Pittsburg-Buffalo Co., Pittsburg, Pa.

Fisher, Thomas, Berwind-White Coal Mining Co., Betz Bldg., Philadelphia, Pa.

Page, Wm. N., Gauley Mt. Coal Co., Ansted, W. Va.

Blauvelt, W. H., Semet-Solvay Co., Syracuse, N. Y.

SUB-COMMITTEE NO. 6.

Coals for Cement, Drying, Brick Kilns, Etc.

Orton, Prof. Edward, Ohio State University, Columbus, Ohio.

Hagar, Edward M., Commercial Bank Bldg., Chicago, Ill.

Lesley, R. W., Pennsylvania Bldg., Philadelphia, Pa.

Hutchins, R. G., Jeffrey Mfg. Co., Columbus, Ohio.

Kolsem, J. C., Indiana Coal Op. Association, Terre Haute, Ind.

Mitchell, Robert, Land Title Bldg., Philadelphia, Pa.

Kemmerer, John, Central Bldg., 143 Liberty St., New York, N. Y.

SUB-COMMITTEE NO. 7.

Sampling, Testing and Improvement of Coals.

Randall, D. T., Chairman, U. S. Geological Survey, Pittsburg, Pa.

Haas, Frank, Fairmont Coal Co., Fairmont, W. Va.

Bailey, Edwin G., 93 Broad Street, Boston, Mass.

McCreath, A. S., 121 Market St., Harrisburg, Pa.

Lord, Prof. N. W., Ohio State University, Columbus, Ohio.

Bush, B. F., Continental Trust Bldg., Baltimore, Md.

Wadleigh, F. R., 65 Broadway, New York, N. Y.

Voorhees, S. S., U. S. Geological Survey, Washington, D. C.

Mueller, Frank E., Roberts & Schaefer Co., Old Colony Bldg., Chicago, Ill.

SUB-COMMITTEE NO. 8.

Forms of Contract (deliveries and acceptances of coals)

Taylor, E. H., Chairman, Old Colony Building, Chicago, Ill.

Bement, A., 2114 Fisher Bldg., Chicago, Ill.

Bush, B. F., Continental Trust Bldg., Baltimore, Md.

Murray, Wm. J., Colorado Fuel & Iron Co., Denver, Colo.

Dougherty, P. L., U. S. Treasury, Washington, D. C.

Bushnell, Fred. N., c/o Stone & Webster, 147 Milk St., Boston, Mass.

Clark, D. O., Union Pacific Coal Co., Omaha, Neb.

SUB-COMMITTEE NO. 9.

Educational Work.

Holmes, J. A., Chairman, U. S. Geological Survey, Washington, D. C.

Dudley, Chas. B., Pennsylvania R. R., Altoona, Pa.

Deems, J. F., N. Y. C. & H. R. R., New York, N. Y.

Wadleigh, F. R., 65 Broadway, New York, N. Y.

Moldenke, Richard, New York, N. Y.

Lathrop, W. A., 108 South Fourth St., Philadelphia, Pa.

Scholz, Carl, Old Colony Building, Chicago, Ill.

Storrs, L. S., New England Inv. & Security Co., Springfield, Mass.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

London, 1909.

WEDNESDAY EVENING, MAY 26TH.

Reception by the Lord Mayor and Corporation of the City of London at the Guildhall. (Leveé, Uniform, or Evening Dress.)

THURSDAY, MAY 27TH.

10 A.M.—Meeting of the Joint Organizing Committee.

3 P.M.—Inaugural Meeting, opened by H. R. H. The Prince of Wales, in the Royal Albert Hall. (Morning Dress.)

EVENING.—Reception by the Foreign Office. (Evening Dress.)

FRIDAY, MAY 28TH.

10 A.M. TO 1.30 P.M.—Sectional Meetings.

2.30 P.M.—General Lectures by Professors Haller and Paterno.

EVENING.—Banquet at the Crystal Palace. (Evening Dress.)

SATURDAY, MAY 29TH.

10 A.M. TO 2 P.M.—Sectional Meetings.

AFTERNOON.—Garden Party at the Botanic Gardens by the Ladies' Committee.

EVENING.—Reception by the London Section of the Society of Chemical Industry at the University of London. (Evening Dress.)

MONDAY, MAY 31ST.

10 A.M. TO 1.30 P.M.—Sectional Meetings.

2.30 P.M.—General Lecture by Prof. O. N. Witt.

4 TO 6 P.M.—Sectional Meetings.

EVENING.—Private Receptions. (Evening Dress.)

TUESDAY, JUNE 1ST.

10 A.M. TO 1.30 P.M.—Sectional Meetings.

2.30 P.M.—General Lecture by Sir Boverton Redwood.

4 TO 6 P.M.—Sectional Meetings.

EVENING.—Reception at the Natural History Museum. (Evening Dress.)

WEDNESDAY, JUNE 2ND.

10 A.M.—Official Closing Meeting of the Congress.

AFTERNOON.—Visit to Windsor Castle, by permission of the King.

UTAH SOCIETY OF ENGINEERS.

On February 19th the Utah Society of Engineers held a public meeting in the hall of the Packard Library, Salt Lake City, for the purpose of discussing the conservation of the natural resources in the intermountain country. Addresses were made by Mr. Clyde Leavitt, U. S. Forest Service, on "Forestry;" Mr. Markham Cheever, Telluride Power Co., on "Water Power;" Mr. William D. Livingston, Irrigated Lands Co., on "Irrigation;" Dr. Robert H. Bradford, University of Utah, on "Mineral Resources;" Mr. Daniel Harrington, formerly of the Utah Fuel Co., on "Fuel Supply;" Mr. E. C. Lackner, Telluride Power Co., on "Water Power from the Standpoint of the Small User;" and Mr. R. W. Saulisbury, Utah delegate to the Conservation Congress. At the March meeting of the Society, held at the University of Utah, papers upon "The Sewer System of Salt Lake City," and "The Filing System in Use in the City Engineer's Office" were read by Messrs. L. H. Krebs and O. H. Skidmore, assistant city engineers. At the annual meeting and banquet, held at the Commercial Club on April 16th, J. F. Merrill, University of Utah, was re-elected *president*; William Ashton, chief engineer Oregon Short Line, *first vice-president*; L. C. Kelsey, city engineer of Salt Lake city, *second vice-president*; D. McNicol, local manager of the Postal Telegraph Co., *secretary*; and J. P. Hornung, resident engineer for the Schott heating system, *treasurer*.

The Fink smelter and smelting process will be explained by Mr. Fink at the May meeting of the Society.

UTAH ACADEMY OF SCIENCE.

The annual sessions of the Utah Academy of Science were held in Salt Lake City on April 9th and 10th, at the Packard Library. The first session was devoted to papers upon Darwin and the factors of evolution in botany and zoology; and at the second session the regular papers were presented. Officers for the year were elected as follows: *President*, W. C. Ebaugh, Univ. of Utah; *First Vice-president*, E. D. Ball, Agric. Col. of Utah; *Second Vice-president*, W. D. Neal; *Secretary*, A. O. Garrett, S. L. H. S.; *Treasurer*, Philomena Homer, B. Y. U.; and *Members of the Council*, W. W. Henderson, B. Y. C., J. L. Gibson, U. of U., and S. H. Goodwin, Proctor Academy.

PERSONAL NOTES.

The Arthur D. Little Laboratory announces the reorganization of the coal department with the following personnel:

Dwight T. Randall, M. E.—Engineer in Charge.

Graduate in Mechanical Engineering, University of Illinois. Formerly with R. W. Hunt & Company; Westinghouse, Church, Kerr & Company; in charge of Steam En-

gineering Laboratory, University of Illinois; in charge of steam boiler tests, United States Government Exhibit, St. Louis Exposition; Engineer in charge of fuel tests, Technologic Branch, United States Geological Survey, directing fuel tests, boiler tests, smoke abatement work and gas producer tests.

Perry Barker, M.S.—Assistant Chemical Engineer.

Graduate in Chemical Engineering, University of Illinois; formerly Chemist Peabody Coal Co., Chicago; Research Chemist Illinois State Engineering Experiment Station; Asst. Engineer U. S. Geological Survey at Fuel Testing Plants, St. Louis and Jamestown; later at Experimental Gas Plant, Ann Arbor, in charge of Tests of Gas Coals.

Karl M. Way, E.M.—Assistant Mining Engineer.

Graduate in Mining Engineering, Ohio State University; formerly Assistant Engineer, Fuel Testing Branch, U. S. Geological Survey, engaged in mine inspection, mine sampling, and studies of coal preparation in all important coal fields of the United States.

Charles H. Jumper, B.S.—Assistant Chemist.

Graduate in Chemistry, Rose Polytechnic Institute; formerly with Testing Departments, Pennsylvania and Union Pacific Railroads.

Homer F. Braddock, B.S.—Assistant Chemist.

Graduate in Chemistry, Pennsylvania State College; formerly with Testing Department, Fairmont and Consolidation Coal Companies.

Arthur D. Camp, A.B.—Asst. Gas Chemist and Engineer.

Graduate in Chemistry, Cornell University; formerly Chemist, Mineral Point Zinc Co.; Asst. Superintendent People's Gas Light & Coke Co., Chicago.

Prof. Chas. Baskerville, Director of the Chemical Laboratory, College of the City of New York, sailed for London on May 15th on the steamer Kroonland, to attend the Seventh International Congress of Applied Chemistry. He will be abroad all summer.

R. D. Rhodes, Supt. of the Bingham Junction plant of the U. S. Smelting & Refining Company, has been compelled on account of ill health to retire temporarily from his duties, and Mr. George Metcalf, formerly Asst. Supt. of the Bingham Junction plant, and recently Superintendent of the Yampa Smelter, is now Acting Superintendent for the U. S. Company.

The Chemistry and Metallurgy Class of the Association Institute, conducted by the Y. M. C. A. of Salt Lake City, has been giving a series of public lectures upon Mining Theory and Practice. The following are the subjects and speakers:

April 6.—Geology of Utah, Dr. Fred. J. Pack, University of Utah.

April 12.—"The Bingham Mines," Mr. Louis Cates, Supt. Boston Con. Mine.

April 20.—"Park City Mines," Mr. P. L. Williams, Jr., Gen. Supt. Daly-West and Daly-Judge Mines.

April 27.—"Milling and Concentrating," H. P. Saunders, Consulting Engineer, Salt Lake City.

May 4.—"Copper Smelting," Mr. E. P. Mathewson, Gen. Supt. Anaconda Mining Co.

May 11.—"Lead Smelting," Mr. A. H. Richards, Asst. Supt. A. S. & R. Co. Smelter, at Murray, Utah.

May 18.—"Mining Law," Mr. Frank B. Stephens, Attorney-at-Law, S. L. C.

May 25.—"Mining Stocks," Mr. W. H. Tibbals, Stock Broker, S. L. C.

On Monday, April 5, 1909, the St. Louis Chemical Society sustained a great and painful loss in the death of Mr. Henry August Hunicke, a man whose true worth, untiring energy, enthusiasm and high ideals could be little appreciated except by those associated with him in his scientific pursuits. Mr. Hunicke was born in St. Louis September 21, 1861.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, 908 G. Street, N. W., Washington, D. C.

908,603. **Method of Treating Electrolytic Slimes for the Recovery of Metals Therefrom.** ALEXANDER J. MCNAB, Trail, British Columbia, Canada. January 5, 1909.

The method consists in converting one or more of the metals of the slime into soluble sulfids; separating the soluble sulfids, in solution, from the residue; roasting the residue and converting more or less silver therein into sulfate, in solution and precipitating metallic silver from such solution.

908,696. **Method of Making Sulfuric Acid.** HUGO PETERSEN, Wilmersdorf, Germany. January 5, 1909.

The method consists in generating sulfurous acid gases, passing them in contact with two supplies of nitrous vitriol of different strength in two separate steps, thereby forming two different supplies of glover acid, submitting the escaping gases to lead chamber action, treating and absorbing the escaping gases which then contain oxids of nitrogen, in two separate steps with the two previously obtained glover acids, thereby producing two separate supplies of nitrous vitriol and separately treating a new supply of sulfurous acid gases with each of the two supplies of nitrous vitriol.

908,925. Manufacture of **Rubber.** MEYER WILDERMAN, London, England. January 5, 1909.

This is a process for separating rubber by treating it with a mixture of solvents, of which one when alone is a solvent of all the constituents of the rubber, while another when alone is only a solvent of resins, the mixture being capable of penetrating the whole of the rubber but only a solvent for a part; running off the mixture of solvents containing the inferior constituents of the rubber; evaporating the mixed solvents from the whole of the rubber and resins, first at atmospheric pressure and then under vacuum; and recovering the mixed solvents without separation from the whole of the rubber and resins.

909,167. **Waterproofing-paint for Portland Cement Buildings.** THOMAS A. EDISON, Llewellyn Park, Orange, N. J. January 12, 1909.

The paint comprises a petroleum residue known as "B. S." dissolved in a suitable solvent, and boiled linseed oil also dissolved in a solvent.

909,168. Waterproofing Fibers and Fabrics. THOMAS A. EDISON, Llewellyn Park, Orange, N. J.

The fiber is impregnated with the petroleum residue known as "B. S."

909,169. Waterproofing Paint for Portland Cement Structures. THOMAS A. EDISON, Llewellyn Park, Orange, N. J. January 12, 1909.

The paint is produced by dissolving the petroleum residue known as "B. S." in petroleum benzin and removing the insoluble portion.

909,171. Magnesia Cement. CARLETON ELLIS, Larchmont, N. Y. January 12, 1909.

This cement is a dry substantially non-hydroscopic powder, comprising oxid of magnesium and saline bodies capable of gradually reacting in the simultaneous presence of water, and said oxid to form chlorid of magnesium; whereby setting qualities are conferred upon the composition, due to the formation of oxychlorid of magnesium.

909,257. Method of Producing Cellulose Threads. EDMUND THIELE, Brussels, Belgium. January 12, 1909.

The method consists in permitting a concentrated solution of cellulose in ammoniac copper to issue from comparatively wide apertures into a slowly acting precipitation bath, drawing out the threads so formed in this bath, and subsequently treating them with a boiling caustic lye.

909,277. Sulfur Color and Process of Making Same. EMILE T. BUNDSMAN, Point Loma, Cal. January 12, 1909.

The dye is made by heating together a mixture of grape sugar, meta-nitranilin, and a sulfuring agent.

909,343. Manufacture of Tanning Extracts. DONALD STEWART, Iverness, Scotland. January 12, 1909.

The extracts are made by passing successively through vats or pits containing tannin-containing material waste sulfite liquor whose ash contains not more than 6 per cent. of iron calculated as FeO, and then settling out difficultly soluble substances and concentrating the clear liquor.

909,536. Composition of Matter for Generating Hydrogen. GEORGE F. BRINDLEY, Niagara Falls, Ontario, Canada. January 12, 1909.

The composition contains sodium, an inert substance and an agent for temporarily preventing the oxidation of the sodium.

909,546. Smokeless Gunpowder. CONRAD P. H. CLAESSEN, Wilmersdorf, Germany. January 12, 1909.

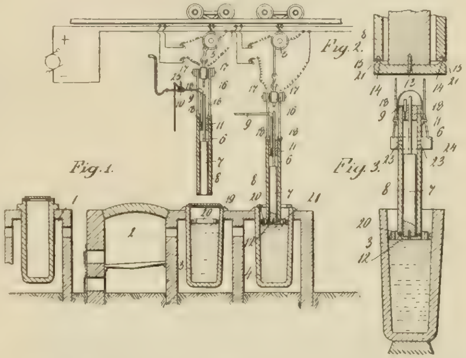
The powder consists of a mixture of nitrocellulose and nitroglycerin with about 5 per cent. diethyldiphenyl-caramid.

909,667. Process of Obtaining Nickel from Silicious Ores. EDGAR F. PRICE, Niagara Falls, N. Y. January 12, 1909.

This is a process of producing ferro-nickel by smelting a charge containing a silicious ore of nickel and iron and carbon by means of an electrically-heated resistance-conductor, withdrawing the slag and product from the furnace and supplying the charge-mixture as required.

909,924. Compound Metal Body and Process of Producing Same. JOHN F. MONNOT, New York, N. Y. January 19, 1909.

In the practice of this method, a bar of aluminum is cleaned thoroughly, and is then heated under conditions precluding oxidation. This heat may be just enough to insure a dry surface, or it may be somewhat higher. The bar, or ingot, is then withdrawn under conditions precluding oxidation and other surface deterioration, and is then plunged momentarily into a bath of silver, copper, or other suitable metal of relatively high melting point, preferably a metal which is not readily oxidizable, such metal being maintained in a very fluid condition, and preferably heated considerably above its melting point. If only a thin coating of copper or other coating metal is desired, the ingot may be withdrawn after a few seconds, under conditions pre



cluding oxidation, and allowed to cool; and when cool will be found to be coated with a thin cohering film of the coating metal having the desirable properties of a metal solidified from the fluid state. Such coating so formed is very thin. If a thicker coating is desired such coating may be formed by confining a portion of the molten metal, of suitable thickness, in contact with the surface of the aluminum body, and then withdrawing the aluminum body, and confined layer and permitting the latter to solidify. The compound ingot thus produced is then preferably worked, as by rolling, pressing, hammering or like mechanical operation.

The illustration shows apparatus for carrying out the process.

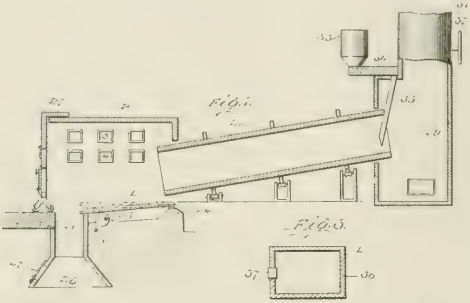
910,049. Composition for Removing Finish. CARLETON ELLIS, Larchmont, N. Y. January 19, 1909.

The remover comprises turpentine with which a metallic resinate has been incorporated and acetone added thereto.

910,121. Process of and Apparatus for Making Cement Clinker. CARLETON ELLIS, Larchmont, N. Y. January 19, 1909.

In this process of making cement clinker, the two operations of calcining and clinkering are more or less segregated, each being performed in apparatus particularly adapted thereto. The calcining is performed in a rotary kiln with the aid of a stream of hot waste gases substantially filling the whole cylinder and therefore contacting with the stream of cement material instead of being spaced away therefrom as in the ordinary kiln, developing the flame yielding the waste gases elsewhere than in this kiln so that there will be no necessity for instituting draft conditions and consequently stratification of gases therein. In some measure,

the sheer temperature required for calcination is reciprocally related to the percentage of carbon dioxid in the gas mass bathing the material being calcined so that in the ordinary operation where the evolved carbon dioxid tends to flow forward over the cement material as a discrete stream under-



lying the hot flame gas stratum, as in the stratified gas currents going through the ordinary kiln, calcination conditions are not as favorable as in the present method, where evolved dioxid is at once diluted in the hot gas mass filling the kiln and bathing the solid cement material.

The hot calcines, free or substantially free, of carbon dioxid, are delivered upon a hearth where such calcines are raised to a clinkering heat, the hearth being heated by any suitable fuel. Waste gases from the hearth chamber, though preferably but a portion of such gases, are passed upward through the rotary kiln to effect calcination in the manner described. It will be noted that the described operation makes calcination and clinkering wholly independent operations though retaining the advantage of the ordinary practice of using but a single source of heat. There is, of course, no necessary relation between the speed of feed of materials through the rotary kiln and the length of time that materials remain on the hearth, and each operation can be independently regulated.

The illustration shows the apparatus in which the process is carried out.

910,524. Process for the Production of Soluble Starch. FERDINAND FRITSCHE, Rumburg, Austria-Hungary. January 26, 1909.

The process consists in mixing common starch with a perborate and heating said mixture.

910,530. Method of Absorbing Oxids of Nitrogen. BIRGER F. HALVORSEN, Christiania, Norway. January 26, 1909.

This method consists in treating the oxids of nitrogen with water and conducting the resulting gases into an absorbent containing caustic alkali and a carbonate of the alkalies.

910,662. Process of Making Caustic Alkalies. WILLIAM T. GIBBS, Buckingham, Quebec, Canada. January 26, 1909.

The process consists in digesting finely divided potash feldspar with milk of lime under steam pressure.

910,707. Process of Treating Iron Ore. CHARLES B. MORGAN, Oakland, Calif. January 26, 1909.

The ore is first melted to a liquid state then a sufficient supply of liquid carbonaceous material is added to effect a reduction of the iron.

910,894. Process of Making Titanium Alloys. FREDERICK M. BECKET, Niagara Falls, N. Y. January 26, 1909.

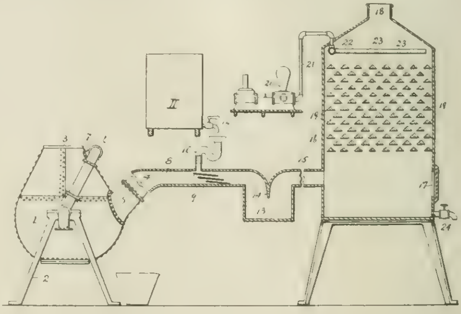
The titanium ore is reduced in an electric furnace by means of carbon in the presence of sufficient silicon to exclude from the product carbon in excess of 10 per cent.

910,936. Dinitroglycerin Explosive and Process of Making. ANTON MIKOLAJAZAK, Kastrop, Germany. January 26, 1909.

The explosive is produced by dissolving gelatinating media in dinitroglycerin and incorporating solid inorganic oxidizing salt, with the mixture.

910,982. Process of Forming Metal Salts. WILLIAM H. ALLEN, Detroit, Mich. January 26, 1909.

In this process furnace gases containing metals in a finely divided or gaseous state, are passed into a retort where a portion is condensed. The gases then pass through a horizontal pipe containing baffle plates over which hydrochloric



or sulfuric acid is allowed to flow, which causes a further separation of metal in the form of chlorids or sulfates. The furnace gases are then passed through a large chamber in which are a number of triangular bars over which water or dilute acid flows to effect a further separation of the melted salts.

911,140. Leather Product and Process for Making the Same. HUGH MACKAY, El Paso, Texas. February 2, 1909.

This is a process of surface hardening sole leather by soaking the same in an aqueous mixture of Portland cement and borax.

911,254. Ammonia-cyanid Process of Treating Ores Containing Precious Metals. DAVID MOSHER, San Francisco, Calif. February 2, 1909.

The process consists in treating copper, nickel, zinc and cobalt ores and tailings with gold and silver values, by simultaneously extracting all the metals with a solution of ammonia and an alkaline earth-metal cyanid.

911,269. Process of Producing Certain Proteids from Buttermilk. LUDWIG H. REUTER, Berkeley, Calif. February 2, 1909.

The process consists in treating buttermilk by neutralizing the acid thereof at a low temperature, then moderately heating for a considerable period of time, then heating for a short time almost to the boiling point, thereafter cooling and filtering and subsequently precipitating the casein.

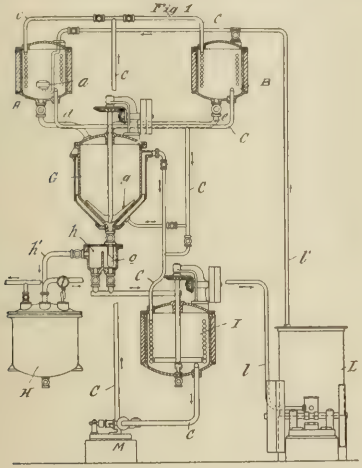
911,283. **Process of Making Fertilizers.** John R. Young, Norfolk, Va. February 2, 1909.

In this process tricalcium phosphate is mixed with undried press-cake of nitrogenous refuse, and potash containing vegetable matter, and the mixture is then decomposed by strong sulfuric acid, the water for the reaction being supplied from the moisture contained in the press-cake of nitrogenous refuse.

911,553. **Process for Purifying Crude Petroleum and Its Distillates.** Lazar Edeleanu, Ployeschi, Roumania. February 2, 1909.

This process consists in treating the crude petroleum, its distillates and its products with sulfur liquefied dioxid. The inventor has discovered that the coloring matters, the disagreeably smelling compounds, and the constituents rich in carbon and poor in hydrogen of the crude petroleum, which injure the quality of the petroleum products, are soluble in liquefied sulfur dioxid, whereas the hydrocarbons

Fig 1



which constitute the refined product are difficulty soluble or altogether insoluble in liquefied sulfur dioxid, supposedly consisting principally of paraffins and naphthenes. This discovery enables the inventor to separate by a physical process the prejudicial constituents of crude petroleum of its distillates merely by using the liquefied sulfur dioxid as a solvent.

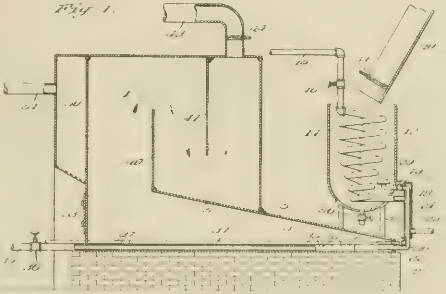
The illustration shows one form of apparatus in which the process can be satisfactorily carried out.

911,606. **Surface Finish.** Percy Neymann, Chicago, Ill. February 9, 1909.

The composition consists of wax, a solvent, coloring matter, and an ingredient for hardening the superficial wax, composed of flowers of sulfur, butter of antimony, and acetic acid.

911,735. **Process of Making Sulfur Dioxid.** Chester W. Lyman, New York, N. Y. February 9, 1909.

This invention relates to a new method of burning sulfur to produce sulfur dioxid and consists essentially in introducing the melted sulfur in the form of spray into a suitable retort and there burning it. The melted sulfur and air are introduced under pressure through nozzles so arranged that the air jet impinges on the inflowing sulfur, whereby the



sulfur is atomized, and at once intimately mixed with the air within the retort. This process is stated to possess the advantage of effecting the result of intimately mixing the sulfur and the air, whereby there is obtained practically perfect combustion of the sulfur and the combination therewith of a larger proportion of the oxygen of the air than usually obtained.

The illustration shows the apparatus in which the process is carried out.

912,245. **Solder for Incandescent-lamp Filaments.** Hans Kuzel, Baden, near Vienna, Austria-Hungary. February 9, 1909.

This means of connecting incandescent lamp filaments to their supply wires, comprises a solder containing carbid of tungsten.

912,266. **Hydraulic Cement.** Arthur C. Spencer and Edwin C. Eckel, Washington, D. C. February 9, 1909.

This is a mixture containing greensand and calcareous material.

OFFICIAL REGULATIONS AND RULINGS.

FOOD INSPECTION DECISION 107.

Decision of the Attorney-General in regard to the legality of the Referee Board.

The decision of the Attorney-General in regard to the legality of the Referee Board is hereby promulgated as Food Inspection Decision No. 107. James Wilson,
Secretary of Agriculture.

Washington, D. C., April 22, 1909.

Department of Justice,
Washington, April 14, 1909.

The Honorable The Secretary of Agriculture.

Sir: I am in receipt of your favor of the 23d ultimo,

asking my opinion with respect to (1) the legality of the appointment by you of five scientific consulting experts to give you necessary advice upon questions arising in the enforcement of the Food and Drugs Act, June 30, 1906, whose salaries and expenses you have directed to be paid from the appropriation "Laboratory, Department of Agriculture" (34 Stat., 1271); and inquiring specifically (2) whether you were, on February 20, 1908, authorized to form these five consulting experts into a board, and to pay the expenses incident to the investigations made by such board at your direction, including the compensation of necessary laboratory helpers, the purchase of materials, etc., and (3) whether section 9 of the sundry civil act, approved March 4, 1909, or any subsequent legislation has impaired the legal status of the appointments and of the organization of the board, or affected the right of the experts so appointed and organized, to receive compensation for their individual services, or affected your powers to a point assistants, laboratory helpers, etc., to assist the members of the board, and to incur expenses for necessary material, etc., all to be paid until June 30, 1909, from the appropriation "Laboratory, Bureau of Chemistry, 1909" (35 Stat., 260), and subsequently from the appropriation "General Expenses, Bureau of Chemistry, 1910" (act entitled "An act making appropriations for the Department of Agriculture for the fiscal year ending June thirtieth, nineteen hundred and ten," approved March 4, 1909).

1. As to the legality of the appointment. The Food and Drugs Act, after prohibiting the introduction into any State or Territory, or the District of Columbia, from any other State or Territory or the District of Columbia, or from any foreign country, or shipment to any foreign country of any article of food or drugs which is adulterated or misbranded, within the meaning of the act, enacts in Section 2:

That the Secretary of the Treasury, the Secretary of Agriculture, and the Secretary of Commerce and Labor shall make uniform rules and regulations for carrying out the provisions of this act, including the collection and examination, of specimens of foods and drugs manufactured or offered for sale in the District of Columbia, or in any Territory of the United States, or which shall be offered for sale in unbroken packages in any State other than that in which they shall have been respectively manufactured or produced, or which shall be received from any foreign country, or intended for shipment to any foreign country, or which may be submitted for examination by the chief health, food, or drug officer of any State, Territory, or the District of Columbia, or at any domestic or foreign port through which such product is offered for interstate commerce, or for export or import between the United States and any foreign port or country.

Section 3 enacts:

That the examinations of specimens of foods and drugs shall be made in the Bureau of Chemistry of the Department of Agriculture, or under the direction and supervision of such Bureau, for the purpose of determining from such examinations whether such articles are adulterated or misbranded within the meaning of this Act; and if it shall appear from any such examination that any of such specimens is adulterated or misbranded within the meaning of this act, the Secretary of Agriculture shall cause notice thereof to be given to the party from whom such sample was obtained. Any party so notified shall be given an opportunity to be heard, under such rules and regulations as may be prescribed as aforesaid, and if it appears that any of the provisions of this act have been violated by such party, then the Secretary of Agriculture shall at once certify the facts to the proper United States district attorney. * * * *

The statutes of the United States do not provide for the *creation* of the Bureau of Chemistry in the Department of Agriculture. The *existence* of such Bureau is recognized in the appropriation acts, and in the act entitled "An act to make appropriations for the Department of Agriculture for the fiscal year ending June thirtieth, nineteen hundred and eight" (34 Stat., 1271), under the head of "Bureau of Chemistry" appropriations are made for the salaries of "One chemist, who shall be chief of Bureau," and a certain number of clerks, laborers, messengers, etc., after which, under the subheading of "Laboratory, Department of Agriculture," a lump sum appropriation was made for "necessary expenses in conducting investigations in this Bureau, including * * * work in such investigations, in the city of Washington and elsewhere * * * ; for the employment of additional assistants and chemists, when necessary * * *; to investigate the composition, adulteration, and false labeling, or false branding of foods, drugs, beverages, condiments, and ingredients of such articles, when deemed by the Secretary of Agriculture advisable * * * . For all expenses necessary to carry into effect * * * [the Food and Drugs Act] * * * employing such assistants, clerks, and other persons as the Secretary of Agriculture may consider necessary for the purposes named * * * ." The act of March 4, 1907 (34 Stat., 1280), passed at the same session with the appropriation act above referred to, expressly authorizes the Secretary of Agriculture.—

to make such appointments, promotions, and changes in the salaries, to be paid out of the lump funds of the several bureaus, divisions, and offices of the Department as may be for the best interests of the service: *Provided*, That the maximum salary of any classified scientific investigator in the city of Washington, or other employee engaged in scientific work, shall not exceed three thousand five hundred dollars per annum. And the Secretary of Agriculture is hereby authorized and directed to pay the salary of each employee from the roll of the bureau, independent division, or office in which the employee is working, and no other: *Provided, however*, That details may be made from or to the office of the Secretary when necessary and the services of the person whom it is proposed to detail are not required in that office; and he is further authorized and directed to submit to Congress each year a statement covering all appointments, promotions, or other changes made in the salaries paid from lump funds, giving in each case the title, salary, and amount of such change or changes, together with reasons therefor. (34 Stat., 1280).

Pursuant to the provisions of Section 2 of the Food and Drugs Act, the Secretary of the Treasury, the Secretary of the Agriculture, and the Secretary of Commerce and Labor, on October 17, 1906, promulgated certain rules and regulations for carrying out the provisions of the act. Regulations 3 and 4 dealt with the collection of samples and the methods of analysis. Regulation 5, "Hearings," is as follows:

(*a*) When the examination or analysis shows that the provisions of the Food and Drugs Act, June 30, 1906, have been violated, notice of that fact, together with a copy of the findings, shall be furnished to the party or parties from whom the sample was obtained or who executed the guaranty as provided in the Food and Drugs Act, June 30, 1906, and a date shall be fixed at which such party or parties may be heard before the Secretary of Agriculture or such other official connected with the food and drug inspection service as may be commissioned by him for that purpose. The hearings shall be private and confined to questions of fact. The parties interested therein may appear in person or by attorney and may propound proper interrogatories and submit oral or written evidence to show any fault or error in the findings of the analyst or examiner. The Secretary of Agriculture may order a reexamination of the sample or have new samples drawn for further examination.

(*b*) If the examination or analysis be found correct the Secretary of Agriculture shall give notice to the United States district attorney as prescribed * * *.

The appropriation act of 1908 (35 Stats., 251, 261) made appropriations for the fiscal year ending June 30, 1909, and contained provisions in the lump sum appropriation for "Laboratory, Department of Agriculture" similar to those above quoted from the act of 1907, except that the sentence "for the employment of additional assistants and chemists" was not included in the enumeration of the objects for which the lump sum appropriation was made.

The appropriation act of 1909 (Public No. 330) contains similar provisions to those above cited from the act of 1908. Under these acts, I am clearly of the opinion that the Secretary of Agriculture was empowered to employ in the Bureau of Chemistry such additional assistants and chemists as he should deem necessary to investigate the composition, adulteration, and false labeling, or false branding of foods, drugs, beverages, condiments, and ingredients of such articles, when deemed advisable by him, and such assistants "and other persons" as he might deem necessary to carry into effect the Food and Drugs Act.

The form of appointment which you made, which accompanies your letter, shows that you appointed each of certain persons "consulting scientific expert to the Secretary of Agriculture, to aid in enforcing the provisions of the" Food and Drugs Act, in the Department of Agriculture at a salary of $25 per day, for days actually employed, to be paid from the appropriation "Laboratory, Department of Agriculture, General Expenses, Bureau of Chemistry," to perform such duties as should be required by the Secretary. While the form of appointment does not expressly specify that the expert is employed as a part of the Bureau of Chemistry, that fact is implied from the specification of the fund from which he is to be paid. In my opinion these appointments were expressly authorized by the acts of Congress referred to.

2. You further inform me that you organized the five persons so appointed into a board called the "Referee Board," and that you imposed upon them the duty to consider and report to you upon the wholesomeness, or the deleterious character of such foods, or of such articles used in foods as you might refer to them. I do not understand from your communication that you conferred upon this so-called Referee Board any *power*. Their sole function was to investigate and report to you, and their detail to your office is justified in the provision of the act of March 4, 1907, above quoted. The purposes for the employment of these gentlemen, and the organization of them by you into a board, are set forth in your letter. You point out that it was to enable you to have recourse to the disinterested and unbiased advice of eminent and expert chemists whenever a serious conflict of opinion may arise as to the deleteriousness of any particular article or substance added to food. It is, of course, apparent that in the administration of a statute of such far-reaching effect as the Food and Drugs Act, the ordinary investigation and conclusions of the Bureau may be disputed by interested parties, and Section 4 of the act provides for a rehearing by the Secretary of Agriculture whenever the conclusion of the Bureau is disputed. The Secretary would naturally desire to reach a right conclusion as to such matters and not subject the owners of articles affected by the ruling to litigation if any error should have been committed by the Bureau, and Congress would seem to have had that in mind in providing in the lump sum appropriations of 1907 and 1908, for the employment of "such assistants, clerks, *and other persons*, as the Secretary of Agriculture may consider necessary for the purposes named," *i. e.*, the investigation of the composition, adulteration, and false labeling, or false branding of foods, drugs, beverages, etc., when deemed by him advisable. Your right to appoint any one of these men for that purpose can scarcely be seriously disputed under the provisions of the act above referred to, and, in my opinion, you were entirely justified in directing them to confer and act as a committee or board in advising you with respect to the enforcement of the act.

3. The act entitled "An act making appropriations for sundry civil expenses of the Government for the fiscal year ending June thirtieth, nineteen hundred and ten, and for other purposes," approved March 4, 1909 (Public No. 328), contains the following provision:

SECTION 9. That hereafter no part of the public moneys, or of any appropriation heretofore or hereafter made by Congress, shall be used for the payment of compensation or expenses of any commission, council, board, or other similar body, or any members thereof, or for expenses in connection with any work or the results of any work or action of any commission, council, board, or other similar body, unless the creation of the same shall be or shall have been authorized by law; nor shall there be employed by detail, hereafter or heretofore made, or otherwise personal services from any executive department or other government establishment in connection with any such commission, council, board, or other similar body.

You inform me that since this enactment a question has been raised as to your right to cause payments to be made to the above-mentioned experts, and you ask my opinion as to whether or not such objections are well founded. In my opinion this section last quoted does not repeal the provisions of the appropriation act passed at the same session, authorizing the Secretary of Agriculture to employ "such assistants, clerks, and other persons as he may consider necessary" to enable him to carry into effect the provisions of the Food and Drugs Act, nor to submit to a number of persons appointed pursuant to that act, to consider

jointly as a committee or board, and report to him for his information, any question upon which he is by law required to take action arising under that act. The commissions or boards referred to in Section 9 of the act of March 4, 1909, are commissions or boards constituted without authority of law, and I can not conceive that it could ever be construed to prohibit the head of a Department from submitting to the concurrent investigation and report of several employees of his Department any question which he might submit for investigation to any one of them. Inasmuch, therefore, as the employment of experts of the character referred to by you is authorized by law, and appropriations made out of which they may be paid for their services, as above set forth, I am of the opinion that neither Section 9 of the sundry civil act, approved March 4, 1909, above referred to, nor any other legislation to which my attention has been called, has affected your right to employ such experts or submit to their joint investigation and report, any question of fact affecting the adulteration or misbranding of articles concerning which any party from whom such articles have been obtained is entitled to be given an opportunity to be heard under the provisions of Section 4 of the Food and Drugs Act.

Respectfully,

GEO. W. WICKERSHAM,
Attorney-General.

The following Judgment Notices have been issued under the Food and Drugs Act:

MARCH 16, 1909.

39. Misbranding of corn and beans (Underweight).
40. Misbranding of canned corn (As to presence of saccharin).
41. Adulteration of water (Great Bear Spring).
42. Misbranding of butter (Renovated butter).

APRIL 12, 1909.

50. Adulteration of coffee (Coated with lead chromate).

APRIL 15, 1909.

51. Misbranding of bottled beer (As to place of manufacture).
52. Misbranding of canned corn (Underweight).
53. Misbranding of canned corn (Underweight).

APRIL 20, 1909.

54. Misbranding of a drug (Muco-Solvent).
55. Misbranding of coffee (As to geographical source).

MAY 7, 1909.

56. Misbranding of lemon extract (As to presence of oil of lemon).
57. Misbranding of canned apples (Underweight).

(T. D. 29701). *Chrome Alum.*

KUTTROFF *v.* UNITED STATES.

U. S. Circuit Court of Appeals, Second Circuit. April 13, 1909. No. 154 (suit 5024).

CHROME ALUM—CHEMICAL SALT—"CRUDE STATE."

Chrome alum, which after production has been subjected to a crystallizing process, being thereby freed from incidental impurities, is by reason of this process removed from the provision in paragraph 482, tariff act of 1897, for articles in a "crude state," used in dyeing, and is dutiable as a chemical salt under paragraph 3.

APPEAL from the Circuit Court of the United States for the Southern District of New York.

[Decision in favor of the Government.]

The decision below (T. D. 29003) affirmed a decision by the Board of United States General Appraisers, G. A. 6647 (T. D. 28346), which had affirmed the assessment of duty by the collector of customs at the port of New York on merchandise imported by Kuttroff, Pickhardt & Co.

Curie, Smith & Maxwell (*W. Wickham Smith* of counsel), for the importers.

J. Osgood Nichols, assistant United States attorney, for the United States.

Before LACOMBE, COXE, and WARD, Circuit Judges.

This cause comes here upon appeal from a decision of the Circuit Court, affirming a decision of the Board of General Appraisers, which affirmed the collector. The importation is commercially known as chrome alum, and was classified under paragraph 3, act of 1897, as a "chemical salt." It is concededly a chemical salt, but the importers contend that it is entitled to free entry under paragraph 482:

Articles in a crude state used in dyeing or tanning not specially provided for.

Per CURIAM: The only question in the case is whether the article is "in a crude state." It is derived as a byproduct from the process of manufacturing certain coal-tar colors. In such process chromium sulphate and potassium sulphate are formed, and these two products combined with water constitute chrome alum; but, as the evidence shows, it remains at close of the process, "as a grayish, greenish paste." This seems to be its crude state, but the paste is thereafter treated with sulphuric acid, and from the solution the chrome alum of the importation crystallizes out, being thereby freed from incidental impurities. We concur with the Board and the Circuit Court that chrome alum thus crystallized is not in a crude state.

(T. D. 1483). *Alcohol for Scientific Purposes.*

Alcohol classified and branded as "commercial alcohol" may be withdrawn from bond, free of tax, under the provisions of Section 3297, Revised Statutes, for scientific purposes.

TREASURY DEPARTMENT.

OFFICE OF COMMISSIONER OF INTERNAL REVENUE

Washington, D. C., April 14, 1909.

SIR: In reply to your letter of the 8th instant, requesting that you be advised whether, in view of the reclassification of distilled spirits, "commercial alcohol" may be withdrawn from bond, free of tax, for scientific purposes, under the provisions of Section 3297, Revised Statutes, you are informed that the honorable Attorney-General, to whom this question was recently submitted, holds that spirits as above designated may be so withdrawn for the purpose stated.

Respectfully,

J. C. WHEELER,
Deputy Commissioner.

MR AUGUST E. MUENTER,
Collector First District, San Francisco, Cal.

INDUSTRIAL AND TRADE NOTES.

The completion April 24 of the custom zinc concentrator of former United States Senator W. A. Clark marked an epoch in the mining industry of Butte.

This plant, the first of its kind in the Northwest, will mean the successful and profitable mining of large bodies of low-grade silver-zinciferous ores, in which the mines of Butte abound and which, heretofore, have defied successful treatment. In fact, it is believed that the Clark method of handling zinc ores will in time bring Butte to the front as one of the principal zinc-producing districts in the world, in addition to its enormous copper output.

The Clark concentrator, the result of long and elaborate experiments, will begin receiving custom zinc ores this week, starting on shipments from the Butte & Superior and the Elm Orlu mines. The plant has a capacity of 300 tons of ore a day, and will produce about 125 tons of about 40 per cent. zinc concentrates, carrying in addition about 25 ounces of silver, about 4 per cent. copper and $1 in gold. About two or two and one-eighth tons of crude ore will be concentrated into one ton of product, the grade of the crude ore determining in a measure the degree of concentration.

On May 4th, the Senior Engineering students of the University of Utah leave for their trip of inspection through Utah and neighboring states. The more important mining camps and smelting districts of Utah, Colorado, Montana and Nevada will be visited.

Work is progressing upon the plant of the International Smelting Company at Tooele. Early in April there was held an auction sale of the lots in the new smelter town, and about $100,000.00 worth of property was sold within a few hours. The company is conducting this enterprise along the lines followed at Anaconda, Mont., with so much success.

NITRIC ACID FROM AMMONIA.—OSTWALD-BRAUER PROCESS.

Notes on lecture by Morse, of Harvard, before the American Chemical Society, April 8, 1909

The work on this process started in Ostwald's laboratory at Leipsic but was afterwards given a commercial trial by Griesheim. Brauer afterwards put up works devoted entirely to this process. As finally worked a mixture of air and ammonia gas must pass through a catalyzer which consists of spirally wound sheet platinum of roughened surface. The temperature is held at a very dull red heat. After the reaction is started the temperature takes care of itself. No definite reaction need be given as different oxids of nitrogen may be produced. From the catalyzer the gas passes to condensation chambers. Five condensing towers in series are used. The weak acid is used as a wash water in the first tower. The best acid is drawn from the second tower and usually runs about 60 per cent. HNO_3. 85 per cent. of the nitrogen of ammonia is converted into nitric acid. The nitric acid obtained is treated with ammonia to give ammonium nitrate. This solution is evaporated and dry ammonium nitrate is obtained.

FEDERAL COURT.

Judge William H. Hunt, in the Butte federal court, April 26th, dismissed the bill in the action brought in the name of Fred. J. Bliss against the Anaconda and Washoe companies to close down the great smelting plant at Anaconda. Each side will pay its own costs, which are said to aggregate about half a million dollars. This order disposes of the famous "smoke" case begun three years ago by the farmers of the Deer Lodge Valley, who claimed they were being damaged by the fumes from the smelter, and who demanded an injunction closing down the work. The main issue was decided last February when Judge Hunt denied the injunction.

In supplementary proceedings, however, the court heard testimony on the part of the smelter company with a view to ascertaining whether everything was being done to eliminate the arsenic from the smelter smoke at Anaconda. Counsel for Bliss had an opportunity on April 19th to combat the evidence introduced on Feb. 15th, but offered no proof. Instead, they submitted an offer to arbitrate, provided that the defendants would be bound to include all the farmers who had contributed to the prosecution in the case, Bliss alone being the complainant of record.

Judge Hunt declared the offer to arbitrate wholly irrelevant. He held that the decision in the Highland Boy case in Utah, on which Bliss relied, was not applicable, and that the defendants were doing all that science could suggest to abate the smoke trouble. The decision is entirely in favor of the defendants, and the only relief to which the complainant is entitled, if entitled to any, is through action for damages or other proper suit.

European Zinc Trust.—According to reports appearing in some of the leading European industrial organs, Consul H. Albert Johnson, of Liege, says that an international agreement has been concluded between a number of prominent zinc works, resulting in the organization of what is designated as the "Syndicat des Usines a Zinc."

The limit of production of each one of the firms having been established, the principal clause of the agreement stipulates that should the current price of zinc fall below £19 ($92.46), or should the accumulation of stocks show an unusual increase, the limit of production will be proportionately reduced. If, on the other hand, the current price of zinc continues to be above £19, this limit of production may be increased as arranged in virtue of an agreement between delegates from each group of concerns making up the trust, which includes German, Belgian, and English concerns, although it seems that agreements have not yet been concluded with the last mentioned.

It is asserted that the works of Heritiers Georg von Giesche, a concern that is said to produce one-fifth of the total output of zinc in Silesia, is not included in the new combine, whose main object is to regulate production, but competion from this quarter apparently is not feared. Steps have been taken to induce the five most important zinc works in England to join the trust; as to the zinc works of the United States, it is believed that anything like extensive exports of zinc from that part of the world are too far in the future to meet serious consideration at the present time.

It is rumored that one of the earliest results of the formation of this trust will be an increase in the present price of zinc, such an advance having already been definitely decided upon.

Referring to his former report regarding the formation of a European zinc trust, Consul H. Albert Johnson writes from Liege that it now appears from more recent reports that the organization of a syndicate composed mainly of German zinc manufacturers was concluded the latter part of February under the form of a limited liability company. The capital is said to be $509,400, and the management is placed in the hands of Director-General Lob, of the Hohenlohe Works. The sale of zinc will be effected through the agency of Beer, Sonheimer & Co., the Metal Gesellschaft, of Frankfurt-on-the-Main, and by Aron Hirsch, of Halberstadt. It is stated that this new combine includes a large number of Belgian, French, Dutch, and Austrian works. —*U. S. Consular Report*, March 23, 1909.

Growth of the German Potash Industry.—Consul-General Richard Guenther writes from Frankfort that the potash production of Germany at present represents about 750,000,000 marks ($178,500,000) of capital and employs 28,000 miners and work people. The yearly sales of potash are $24,000,000, the trade being controlled by a trust. In 1908 this combine added 9 new mining companies to its membership, while this year 13 new works will go into operation, and also controlled by the potash trust. Germany alone consumes for soil fertilization nearly half the potash salts annually produced. There has been much speculation among German investors in shares of potash-production companies.—*U. S. Consular Report*, March 25, 1909.

Radium in Cornwall.—A report from Consul Joseph G. Stephens, of Plymouth, states that considerable interest is manifested throughout England in the announcement of the existence in large quantities in Cornwall of pitchblende, from which radium is produced after the extraction of uranium. The consul describes the sources of the valuable article and probability of securing further supplies:

Pitchblende ore is largely found in the Erzgebirge, in Bohemia, and in Cornwall, and so valuable are such finds of pitchblende that the Austrian Government, exercising a legitimate right, has prohibited further export from that country. The world, therefore, must be searched for new sources of supply, and Cornwall appears likely to furnish the deficiency. Portugal has also been mentioned as a likely field.

The process of extraction is extremely tedious and expensive, tons of pitchblende (oxide of uranium) yielding only the minutest quantities of the precious mineral. However, the fact that a pound of radium is theoretically worth over $36,000,000 is an inducement to produce it, and science makes its production a necessity. [The total world production of radium has not yet equaled one gram.—B. of M.] It is known that radium is widely disseminated throughout the earth's crust, but the occurrence of radioactive minerals in a formation sufficiently permanent to render mining at any depth a paying proposition is still very rare. Radium to be appreciably cheaper must be derived from uranium minerals, when obtainable in large quantities from surface deposits at little expense. Even where so found the cost of its separation from other minerals and waste is enormous. Great interest therefore naturally attaches to the refuse heaps at the mines of Cornwall.

The particular mine in which the existence of radium has been found is in the St. Austell district, but St. Ives is sharing the public attention by reason of the investigations which have been made for some time past. At present the Cornish mines are fitted with machinery for dealing with the residuum as ore, but not for dressing it, and persons are engaged to crush it into powder. Their market thus far has been for uranium oxide, which has been sent to Germany, where it is chemically treated to produce sodium uranite for the colored glass and porcelain trade, and nitrate of uranium for the photographic trade. Hitherto the tailings from the mines have been regarded as useless, but it has recently been discovered that the residuum is the mother of radium. The Cornish Company contemplates the establishment of works for the treatment of pitchblende at Trenwith mine, near St. Ives, and in the St. Agnes district. It is asserted that the works will afford employment to some 400 workmen, and will constitute a new industry of considerable benefit to the country.—*U .S. Consular Report*, March 26, 1909.

Nitrate Combine Broken.—Consul Rea Hanna, of Iquique, advises that at a meeting held on March 29, 1909, it was definitely decided to discontinue the combination among the Chilean producers of nitrate of soda, for the control of the production and exportation of that article. The consul writes:

Forty-one producers, representing 77 "officinas" (nitrate works), accepted quotas of production aggregating 40,480,000 Spanish quintals of 101.61 pounds each, and 46 producers, representing 77 officinas, refused to accept the quotas assigned to them. Those refusing to accept demanded quotas aggregating 10,800,000 quintals more than was proposed to them.

As a consequence the nitrate combination ceased to exist on March 31, 1909. In the future, or until a new combination be formed, there will be unlimited production and exportation by the several officinas. This condition is desired by many of the producers who possess rich deposits and whose cost of production is low, and the general opinion is that the nitrate market will suffer at least only a temporary fluctuation as a result. The "Association Salitrera de Propaganda," however, still continues as an advertising medium, and as a statistical department for the industry.—*U. S. Consular Report*, May 10, 1909.

CORRECTION.

On page 300 left-hand column, about the 24th and 25th lines for

"Ground October, 1907" insert "Ground October, 1906."

"Analyzed October, 1907" insert "Analyzed October, 1907."

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ORIGINAL PAPERS

EXPERIMENTS ON THE UTILIZATION OF NITROGEN IN FERTILIZER MATERIALS.

By Edward B. Voorhees and Jacob G. Lipman.

Received May 1, 1909.

Nitrogenous fertilizers possess an agricultural value that is far from constant. A larger or smaller proportion of the nitrogen applied may be returned in the crop, the returns being directly affected by the character of the soil, of the season, and of the crop itself. But while there is a very considerable range of variation in the returns from a given quantity of nitrogenous substance a more or less definite relation still persists that enables us to classify nitrogenous materials according to their *availability*, that is, according to the readiness with which they may be transformed into plant-tissue. Materials like sodium nitrate are designated as readily available because a large proportion of their nitrogen is returned in the crop to which they are applied, while materials like ground leather are designated as slightly available because they yield but little nitrogen under the same conditions.

The entire question of availability, particularly in its relation to nitrogenous fertilizers, is one of extreme importance in all sections where fertilizers are used. Yet, notwithstanding its importance, it is scarcely appreciated by the average user of commercial fertilizers. To him quantity is the only desideratum and he does not inquire as to the source of the nitrogen in the mixed goods that he purchases. On the other hand, the manufacturers of fertilizers are well aware of the comparatively high availability of materials like sodium nitrate, ammonium sulphate, or calcium cyanamid. But they are forced to harmonize as best as they can the conflicting relations between agricultural and commercial values. They realize that these values do not run parallel to one another, since the less readily available forms of plant-food are not always the cheapest, nor the more readily available forms the dearest.

But apart from commercial fertilizers, the availability of nitrogen compounds is a matter that concerns all farmers. Animal manures used so extensively on arable soils show a wide range of availability under varying conditions, and the same holds good with leguminous or non-leguminous green manures. We cannot always account for the variations in availability even though we recognize the composition of the nitrogenous materials, and the character of season, crop and soil as contributing factors. It will not be disputed, however, that in view of the vast economic significance of the nitrogen question in agriculture, a clearer understanding of the factors affecting the availability of nitrogenous fertilizers is highly desirable. It is hoped that the experiments reported in the following pages may serve as a contribution towards the better understanding of availability and its underlying causes.

METHODS EMPLOYED.

The experiments under consideration were carried out in large galvanized iron cylinders 4 feet long and 23.5 inches in diameter, open at both

ends. After being carefully painted both inside and outside the cylinders were sunk into holes dug for the purpose until the upper rim projected about 2 inches above the level of the surrounding soil. The carefully mixed gravelly subsoil was then placed in the cylinders and packed up to about 10 inches of the top. The subsoil was covered in each case with weighed quantities of soil which formed a layer of about 8 inches in depth.

There were secured in this manner sixty small plats containing soil and subsoil of identical composition. In each case the contents of the cylinder were isolated from the adjoining soil to a depth sufficient to exclude external influences. The sixty cylinders were divided into twenty series of three plats each, representing twenty different systems of nitrogen treatment. The three soils in each series received the same treatment, allowing thus a more perfect equalization of experimental error.

The surface soil selected for the experiment corresponds to the type designated in the survey work of the Bureau of Soils as Penn Loam.[1] A sample from the vicinity of New Brunswick examined by the Bureau of Soils was found to possess the following mechanical composition:

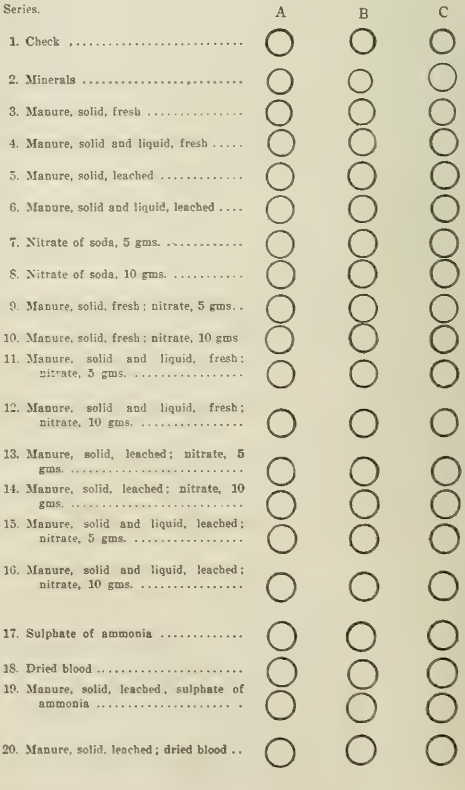
	Mm.		Mm.	Per cent.
Organic matter	.....	to	......	1.38
Gravel	2.000	"	1.0000	3.40
Coarse sand	1.000	"	0.5000	7.20
Medium sand	0.500	"	0.2500	4.50
Fine sand	0.250	"	0.1000	7.58
Very fine sand	0.100	"	0.0500	5.04
Silt	0.050	"	0.0050	41.62
Clay	0.005	"	0.0001	29.62

This soil type represents a large area in the state and is well adapted for the growth of cereals and grasses. A sufficiently large quantity of such soil was gathered in the neighborhood of the station from a field in which no crop had been grown for twenty years or more, and upon which no manure had been applied within the knowledge of those familiar with the land for a long time. In so far as native vegetation is concerned, it was practically barren, and it was supposed that the soil was very poor in nitrogen, and, therefore, well adapted for nitrogen studies. Subsequent analyses showed, however, that this soil was rich in nitrogen. As will be seen later, the comparatively large proportion of nitrogen did not prove detrimental to the satisfactory progress of the experiment.

After sifting and thorough mixing, the soil was distributed in the several cylinders in carefully weighed portions each containing 180 pounds of air-dry soil. All soils in the sixty cylinders received a liberal allowance of lime, and with the exception of those in Series 1, they received also dressings of acid phosphate and of potassium chloride (muriate of potash) at the rate of 640 pounds and 320 pounds per acre, respectively. The application of the phosphorus and potassium compounds has been renewed annually, for a period now of eleven years, with the purpose in view, primarily, of providing an excess of these constituents and of assuring to the nitrogen the rôle of the *controlling* factor in the development of the crops. It may be readily seen, at the same time, that such large applications of acid phosphate and of muriate would constitute a serious drain on the lime in the soil, which drain would be intensified still further in those series where manure, ammonium sulphate

[1] Burke and Wilder, 4th Rep. Field Operations, Bur. Soils, U. S. Dept. Agr., p. 163.

Diagram of Experiment.



and dried blood are applied. It goes without saying that the proportion of lime in the soil, as well as the rate of its removal, play a very essential part in the transformation of soil nitrogen, and, hence, in the economy of its utilization by the crops. This point will be discussed more fully in connection with the crop yields of 1908.

The fertilizer and manure treatment for the different series is shown in the accompanying diagram.

It will be seen that nothing at all was applied in Series 1, and only minerals, that is, acid phosphate and muriate of potash, in Series 2. The nitrogenous materials applied in Series 3–20 in addition to the minerals, included sodium nitrate, ammonium sulphate, dried blood, and four grades of cow manure: *viz.*, solid excreta, fresh; solid and liquid excreta, fresh; solid excreta, leached; and solid and liquid excreta, leached. The nitrate was applied in two different quantities: in the one case at the rate of 5 grams per cylinder, equivalent to 160 pounds per acre, and in the second at the rate of 10 grams per cylinder, equivalent to 320 pounds per acre. The applications of ammonium sulphate and of dried blood contained quantities of nitrogen equivalent to that in the larger application of nitrate. Proper allowance was made for the slighter availability of the nitrogen in the manure by applying quantities of the latter sufficient to furnish about 4 grams of nitrogen, as compared with the 0.78 gram in the 5 grams of nitrate, and the 1.55 grams in the 10 grams of nitrate or in the ammonium sulphate and dried blood.

At the end of each growing season, determinations were made of the actual dry matter in the different crops, of the proportion of nitrogen contained in them, of the gain of nitrogen due to the materials added, and of the per cent. of applied nitrogen recovered. The crops grown in the cylinder soils followed one another in regular rotation and consisted of corn, oats, wheat and timothy. These were the main crops. In some instances the main crops were followed by "residual" crops to which no further applications of manures or fertilizers were made. It was intended that these residual crops gather and lay fast in their tissues the available nitrogen that the main crops failed to take up and assimilate.

The corn which was the first crop in the rotation was not followed by a residual crop, the soil remaining bare in the late fall and winter. The second crop, oats, was succeeded by millet for the accumulation of residual nitrogen. The third crop, oats, was followed by corn as the residual crop. The fourth crop, wheat, had no residual crop grown after it, but was followed directly by timothy. Two cuttings were made of the latter, the second cutting being regarded as the residual crop.

The first rotation began in 1898 and ended in 1902. The three soils in each series were then thoroughly mixed in one heap in order to equalize slight differences that may have arisen in the course of the rotation, and a third of this uniform soil mixture was returned to each cylinder. The same procedure has been followed also in the second rotation except that the second main crop, that is the oats of 1904, was followed by corn instead of millet. The second rotation came to an end in the fall of 1907. In the spring of 1908, the several soils were spaded up and ground limestone at the rate of two tons per acre was applied in 1B–20B and 1C–20C, 1A–20A remaining unlimed. The manures and fertilizers were then applied in the usual way and corn planted in all of the cylinders. The succession of crops in the eleven seasons was therefore as follows:

1898 Corn	1903 Corn
1899 Oats (millet)	1904 Oats (corn)
1900 Oats (corn)	1905 Oats (corn)
1901 Wheat	1906 Wheat
1902 Timothy (two cuttings)	1907 Timothy (two cuttings).
	1908 Corn.

Of the eleven main crops and six residual crops (including the second cuttings of timothy) thus harvested, only three will be considered here; namely, the corn crops of 1898, 1903, and 1908, respectively. The discussion of the analytical data will concern the yields of dry matter, the proportionate content of nitrogen in the dry matter, the yields of nitrogen, the proportion of nitrogen from the different materials recovered in the crop, and the relative availability of the nitrogen in the different materials. The discussion will also concern the influence of the lime applied in 1908 on the yields and composition of the corn crop.

TABLE 1.—RESULTS OF THE CORN EXPERIMENT, 1898.

Series.	Nitrogen applied. Grams	Dry matter in crop. Grams.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
1 A	....	240.2	0.812	1.95	....	.....	.....
B	....	208.0	0.707	1.47	....	.....	.....
C	....	195.8	0.919	1.80	....	.....	.....
2 A	....	289.6	0.625	1.79	....	.....	.....
B	....	253.9	0.527	1.44	....	.....	.....
C	....	329.8	0.722	2.38	....	.....	.....

TABLE I—(*Continued*).

Series.	Nitrogen applied. Grams.	Dry matter in crop. Grams.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
3 A	4.84	323.2	0.684	2.21	0.34	7.02	.....
B	4.84	313.3	0.718	2.25	0.38	7.85	7.44
C	4.84	370.7	0.782	2.90	1.03	*21.28	.....
4 A	5.40	475.0	0.665	3.16	1.29	23.89	.....
B	5.40	467.1	0.634	2.96	1.09	20.19	22.04
C	5.40	450.6	0.679	3.06	1.19	22.04	.....
5 A	4.09	441.3	0.603	2.66	0.79	19.32	.....
B	4.09	340.0	0.682	2.32	0.45	11.01	16.80
C	4.09	378.5	0.711	2.69	0.82	20.06	.....
6 A	4.16	409.6	0.635	2.60	0.73	17.55	.....
B	4.16	358.5	0.561	2.01	0.14	* 3.37	22.36
C	4.16	420.4	0.714	3.00	1.13	27.17	.....
7 A	0.80	332.1	0.717	2.38	0.51	63.75	.....
B	0.80	325.6	0.703	2.29	0.42	52.50	69.58
C	0.80	331.3	0.788	2.61	0.74	92.50	.....
8 A	1.60	360.9	0.632	2.28	0.41	*25.63	.....
B	1.60	393.9	0.624	2.46	0.59	36.88	44.38
C	1.60	396.6	0.678	2.70	0.83	51.88	.....
9 A	5.64	356.4	0.558	1.99	0.12	2.13	.....
B	5.64	343.2	0.653	2.24	0.37	6.57	9.64
C	5.64	388.1	0.776	3.01	1.14	20.22	.....
10 A	6.44	389.5	0.657	2.56	0.69	10.73	.....
B	6.44	394.2	0.629	2.48	0.61	9.49	10.11
C	6.44	405.8	0.823	3.34	1.47	*22.84	.....
11 A	6.20	463.3	0.762	3.53	1.66	26.77	.....
B	6.20	508.6	0.655	3.33	1.46	23.55	24.62
C	6.20	468.3	0.711	3.33	1.46	23.55	.....
12 A	7.00	508.0	0.748	3.80	1.93	27.57	.....
B	7.00	498.0	0.787	3.92	2.05	29.27	30.28
C	7.00	504.5	0.842	4.25	2.38	33.99	.....
13 A	4.89	490.2	0.741	3.63	1.76	*35.99	.....
B	4.89	374.8	0.651	2.44	0.57	11.66	11.56
C	4.89	396.5	0.613	2.43	0.56	11.45	.....
14 A	5.69	512.4	0.710	3.64	1.77	*31.11	.....
B	5.69	426.2	0.737	3.14	1.27	22.32	19.07
C	5.69	415.3	0.667	2.77	0.90	15.82	.....
15 A	4.96	391.2	0.721	2.82	0.95	19.15	.....
B	4.96	359.0	0.591	2.12	0.25	* 5.04	19.76
C	4.96	384.7	0.749	2.88	1.01	20.36	.....
16 A	5.76	361.7	0.868	3.14	1.27	22.05	.....
B	5.76	385.7	0.954	3.68	1.81	*31.42	20.14
C	5.76	419.0	0.697	2.92	1.05	18.23	.....
17 A	1.65	387.8	0.671	2.60	0.73	44.24	.....
B	1.65	401.0	0.631	2.53	0.66	40.00	44.24
C	1.65	330.1	0.809	2.67	0.80	48.48	.....
18 A	1.65	322.2	0.664	2.14	0.27	*19.15	.....
B	1.65	341.8	0.702	2.40	0.53	37.59	42.36
C	1.65	303.7	0.836	2.54	0.67	47.52	.....
19 A	5.74	408.6	0.732	2.99	1.12	19.51	.....
B	5.74	439.2	0.688	3.02	1.15	20.03	21.77
C	5.74	442.0	0.758	3.35	1.48	25.78	.....
20 A	5.74	361.7	0.608	2.20	0.33	* 6.00	.....
B	5.74	376.6	0.754	2.84	0.97	17.64	16.55
C	5.74	410.0	0.663	2.72	0.85	15.46	.....

* Not included in the average.

TABLE II.—RESULTS OF CORN EXPERIMENT, 1903.

Series.	Nitrogen applied. Grams.	Air-dry matter in crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
1 A	....	51	1.632	0.832	.....	....	....
B	....	81	0.941	0.762	.....	....	....
C	....	81	1.113	0.902	.....	....	....
2 A	....	163	0.616	1.004	Ave.	....	....
B	....	148	0.607	0.898	(0.991)	....	....
C	....	170	0.630	1.071	.....	....	....
3 A	4.00	205	0.647	1.326	0.335	8.4	....
B	4.00	217	0.673	1.460	0.469	11.7	9.0
C	4.00	202	0.629	1.271	0.280	7.0	....
4 A	3.99	351	0.524	1.839	0.848	21.3	....
B	3.99	315	0.541	1.704	0.713	17.9	20.7
C	3.99	321	0.594	1.907	0.916	23.0	....
5 A	3.97	262	0.537	1.407	0.416	10.5	....
B	3.97	267	0.554	1.479	0.488	12.3	13.7
C	3.97	273	0.629	1.717	0.726	18.3	....
6 A	4.00	238	0.655	1.559	0.568	14.2	....
B	4.00	265	0.594	1.574	0.583	14.6	15.1
C	4.00	249	0.664	1.653	0.662	16.6	....
7 A	0.78	186	0.656	1.220	0.229	29.4	....
B	0.78	189	0.609	1.151	0.160	20.5	25.0
C	0.78	215	0.633	1.361	0.370	*47.4	....
8 A	1.55	255	0.651	1.660	0.669	43.2	....
B	1.55	183	0.752	1.376	0.385	24.8	35.0
C	1.55	245	0.638	1.563	0.572	36.9	....
9 A	4.78	304	0.638	1.940	0.949	19.9	....
B	4.78	254	0.743	1.887	0.896	18.7	19.1
C	4.78	288	0.656	1.889	0.898	18.8	....
10 A	5.55	366	0.621	2.273	1.282	23.1	....
B	5.55	424	0.559	2.370	1.379	24.8	22.8
C	5.55	371	0.573	2.126	1.135	20.4	....
11 A	4.77	319	0.581	1.853	0.862	18.1	....
B	4.77	372	0.605	2.251	1.260	26.3	22.6
C	4.77	388	0.542	2.103	1.112	23.3	....
12 A	5.54	432	0.621	2.683	1.692	30.5	....
B	5.54	445	0.537	2.390	1.399	25.3	27.1
C	5.54	424	0.567	2.404	1.413	25.5	....
13 A	4.75	256	0.572	1.464	0.473	10.0	....
B	4.75	282	0.559	1.576	0.585	12.3	12.8
C	4.75	313	0.563	1.762	0.771	16.2	....
14 A	5.52	436	0.489	2.132	1.141	20.7	....
B	5.52	400	0.497	1.988	0.997	18.1	19.1
C	5.52	388	0.519	2.014	1.023	18.5	....
15 A	4.78	299	0.598	1.788	0.797	16.7	....
B	4.78	308	0.602	1.854	0.863	18.1	17.2
C	4.78	304	0.589	1.791	0.800	16.7	....
16 A	5.55	413	0.554	2.288	1.297	23.4	....
B	5.55	383	0.563	2.156	1.165	21.0	23.1
C	5.55	333	0.711	2.368	1.377	24.8	....
17 A	1.62	317	0.523	1.658	0.667	41.2	....
B	1.62	291	0.500	1.455	0.464	28.6	34.9
C	1.62	251	0.509	1.278	0.287	*17.7	....

* Not included in the average.

TABLE II (*Continued*).

Series.	Nitrogen applied. Grams.	Air-dry matter in crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
18 A	1.55	235	0.566	1.330	0.339	21.9	....
B	1.55	216	0.566	1.223	0.232	15.0	20.7
C	1.55	225	0.614	1.382	0.391	25.2	....
19 A	5.59	405	0.523	2.118	1.127	20.2	....
B	5.59	412	0.492	2.027	1.036	18.5	18.8
C	5.59	378	0.523	1.977	0.986	17.6	....
20 A	5.52	355	0.570	2.024	1.033	18.7	....
B	5.52	321	0.535	1.717	0.726	13.2	16.3
C	5.52	354	0.547	1.936	0.945	17.1	....

TABLE III.—RESULTS OF THE CORN EXPERIMENT. 1908.

Series.	Nitrogen applied. Grams.	Air-dry matter in crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams.	Per cent. of nitrogen recovered.	Average. Per cent.
1 A	....	65	0.857	0.557	.....	.....	.....
B	....	94	0.711	0.668	.....	.....	.....
C	....	125	0.679	0.848	.....	.....	.....
2 A	....	150	0.547	0.820	.....	.....	.....
B	....	169	0.528	0.892	.....	.....	.....
C	....	176	0.540	0.950	.....	.....	.....
3 A	4.00	224	0.558	1.249	0.362	9.05	.....
B	4.00	263	0.543	1.428	0.541	13.52	11.20
C	4.00	248	0.536	1.329	0.442	11.05	.....
4 A	4.00	340	0.441	1.499	0.612	15.30	.....
B	4.00	326	0.482	1.571	0.684	17.10	17.55
C	4.00	373	0.455	1.697	0.810	20.25	.....
5 A	4.00	236	0.528	1.246	0.359	8.97	.....
B	4.00	249	0.540	1.344	0.457	11.42	11.77
C	4.00	289	0.514	1.485	0.598	14.95	.....
6 A	4.00	254	0.482	1.224	0.337	8.32	.....
B	4.00	259	0.477	1.235	0.348	8.70	11.50
C	4.00	278	0.569	1.581	0.694	17.35	.....
7 A	0.78	188	0.496	0.932	0.045	5.80	.....
B	0.78	228	0.492	1.121	0.234	30.00	25.26
C	0.78	249	0.482	1.200	0.313	40.13	.....
8 A	1.55	257	0.506	1.300	0.413	26.65	.....
B	1.55	331	0.470	1.555	0.668	43.10	37.35
C	1.55	332	0.465	1.543	0.656	42.32	.....
9 A	4.78	288	0.533	1.535	0.648	13.56	.....
B	4.78	307	0.506	1.553	0.666	13.93	16.74
C	4.78	386	0.511	1.972	1.085	22.69	.....
10 A	5.55	383	0.455	1.742	0.855	15.41	.....
B	5.55	444	0.460	2.042	1.155	20.81	16.32
C	5.55	312	0.511	1.594	0.707	12.74	.....
11 A	4.78	418	0.499	2.085	1.198	25.06	.....
B	4.78	497	0.514	2.554	1.667	34.87	30.40
C	4.78	491	0.485	2.381	1.494	31.25	.....
12 A	5.55	459	0.452	2.074	1.187	21.39	.....
B	5.55	483	0.492	2.376	1.489	26.83	27.10
C	5.55	538	0.506	2.722	1.835	33.06	.....
13 A	4.78	296	0.506	1.479	0.592	12.38	.....
B	4.78	530	0.499	2.644	1.757	*36.76	22.01
C	4.78	328	0.511	1.676	0.789	16.51	.....

* Not included in the average.

TABLE III—(*Continued*).

Series.	Nitrogen applied. Grams.	Air-dry matter in crop. Grams.	Nitrogen in air-dry matter. Per cent.	Nitrogen in crop. Grams.	Increase over check plot. Grams	Per cent. of nitrogen recovered.	Average. Per cent.
14 A	5.55	379	0.460	1.743	0.856	15.42	.....
B	5.55	450	0.445	2.002	1.115	20.10	18.11
C	5.55	417	0.463	1.930	1.043	18.80	.....
15 A	4.78	296	0.521	1.542	0.655	13.69	.....
B	4.78	304	0.497	1.511	0.624	13.05	14.67
C	4.78	315	0.543	1.710	0.823	17.22	.....
16 A	5.55	386	0.477	1.841	0.954	17.19	.....
B	5.55	432	0.477	2.060	1.173	21.13	19.57
C	5.55	412	0.490	2.018	1.131	20.38	.....
17 A	1.62	239	0.542	1.295	0.408	25.19	.....
B	1.62	286	0.449	1.284	0.397	24.51	27.90
C	1.62	291	0.494	1.437	0.550	33.95	.....
18 A	1.57	182	0.597	1.086	0.199	12.68	.....
B	1.57	228	0.580	1.322	0.435	27.71	24.78
C	1.57	245	0.580	1.421	0.534	34.01	.....
19 A	5.62	317	0.565	1.791	0.904	16.10	.....
B	5.62	348	0.546	1.900	1.013	18.02	17.86
C	5.62	366	0.542	1.983	1.096	19.50	.....
20 A	5.57	248	0.563	1.397	0.510	9.15	.....
B	5.57	300	0.606	1.818	0.931	16.71	15.31
C	5.57	346	0.580	2.006	1.119	20.10	.....

THE RETURNS IN THE CORN CROPS OF 1898, 1903, AND 1908.

The crop of 1908 was in some respects abnormal, for it contained much larger quantities of dry matter and of nitrogen than were present in any of the following crops. This is readily explained by the fact that the stirring and aeration of the soil incident to sifting, mixing and weighing intensified oxidation processes to a very marked extent and made available comparatively large amounts of nitrogen and of other constituents of plant food. For the same reason the influence of the different nitrogenous materials applied in 1898 was not as consistently apparent as it was in the succeeding years. For instance in 6B only 3.37 per cent. of the nitrogen applied was recovered in the crop; in 9A only 2.13 per cent., in 9B only 6.57 per cent., etc. A comparison of Tables I, II and III will show, however, that the soils in each series yielded results which, in most cases, agree satisfactorily among themselves.

By taking the averages for the several series we are permitted to see more clearly the influence of the different methods of treatment already outlined in the foregoing pages.

The data included in Table IV show the average yields of dry matter for the three seasons under consideration. They also show the yields of dry

matter in the unlimed soils 1A–20A and the limed soils 1B–20C for the season 1908.

Table IV.—The Average Yields of Dry Matter in 1898, 1903 and 1908.

Series.	1898, gms.	1903, gms.	1908, gms.	1908, A's, gms.	1908, B's and C's, gms.
1	214.7	71.0	94.7	65.0	109.5
2	291.1	160.3	165.0	150.0	172.5
3	335.7	208.0	245.0	224.0	255.5
4	464.2	329.0	346.3	340.0	349.5
5	386.6	234.0	258.0	236.0	269.0
6	396.2	250.7	263.7	254.0	268.5
7	329.7	196.7	221.7	188.0	238.5
8	383.8	227.7	306.7	257.0	331.5
9	362.6	282.0	327.0	288.0	346.5
10	396.5	387.0	379.7	383.0	378.0
11	480.1	359.7	468.7	418.0	494.0
12	503.5	433.7	493.3	459.0	510.5
13	420.5	283.7	312.0	296.0	329.0
14	451.3	408.0	415.3	379.0	433.5
15	378.3	303.7	305.0	296.0	309.5
16	388.8	376.3	410.0	386.0	422.0
17	373.0	286.3	272.0	239.0	288.5
18	322.6	225.3	218.3	182.0	236.5
19	429.9	398.3	343.7	317.0	357.0
20	382.8	347.3	298.0	248.0	323.0

Taking the average yields of 1898 and 1903, as well as those on the unlimed soils in 1908, as given in the fourth column of Table IV, we note the very marked decline in the yields of Series 1. In 1898, the weight of the dry matter was 214.7 grams; in 1908 it was only 65.0 grams. The decrease in the other series, from 1898 to 1903, was very marked. From 1903 to 1908 there was a decrease in some series and an increase in others, the differences being comparatively small in most instances. We may note, however, that the decrease occurred in Series 1, 2, 7, 10, 14, 15, 17, 18, 19 and 20; and the increase in Series 3, 4, 5, 6, 8, 9, 11, 12, 13 and 16. The decrease in Series 1 and 2 may be readily explained by the failing supply of phosphoric acid and of nitrogen, respectively. The decrease in Series 17, 18, 19 and 20 may be explained by the accumulation of acidity in the corresponding soils, and the decrease in Series 7 by the diminishing supply of available nitrogen in the soil. On the other hand, the increase occurred in the series that have been receiving applications of manure, or of manure and nitrate together. At the same time, it should not be assumed that the ability of the different soils to supply available nitrogen to the crops had increased from 1903 to 1908. As will be shown later, the crops of 1908 contained a smaller proportion of nitrogen, and the yields of total nitrogen in that year were therefore smaller than those of 1903.

As to the influence of the several methods of nitrogen treatment, we may conveniently compare the influence of the fresh manures when used alone or in combination with nitrate with the influence of the leached manures when similarly used. We may likewise compare the action of the small and large applications of nitrate when used alone or in combination with manure, and the influence of nitrate, ammonium sulphate and dried blood when used alone or in combination with manure.

In making these comparisons we note, in the first place, that all of the applications of nitrogen in Series 3–20 resulted in an increased crop yield as compared with Series 2 where minerals alone were employed. In Series 4 where solid and liquid, fresh, was used the yield of dry matter was invariably larger than those in Series 3 where solid, fresh, was used. The superiority of the solid and liquid portion is also apparent in the combinations with nitrate, for we find the yields in Series 11 larger than those in Series 9, and the yields in Series 12 larger than those in Series 10.

The corresponding differences in the leached manures are not so marked. To be sure, when used alone, the solid and liquid leached gave somewhat higher returns than the solid, leached. But when these manures were used in combination with nitrate the corresponding relations were frequently reversed, as may be seen by comparing Series 13 and 15 and Series 14 and 16.

Comparing the returns from the fresh and leached manures, we observe that the solid, fresh, on the one hand, and the two leached manures, on the other, were not markedly different in their influence on the crop-yields. On the other hand, the solid and liquid, fresh, when used alone or in combination with nitrate proved to be decidedly superior to either of the leached manures. This should have been expected from the fact that the solid and liquid, fresh, contained a large proportion of amino compounds, readily nitrifiable, and, therefore, readily available to the growing plants.

The relative influence of the small and large applications of nitrate is consistently maintained in Series 7 and 8 where it was used alone and in Series 9–16 where it was used in combination with the different manures. Comparing Series 9, 11, 13 and 15 with the corresponding even Series 10, 12, 14 and 16, we note that the larger application of nitrate almost invariably surpassed the corresponding smaller application. We may take it for granted, therefore, that nitrogen was really the controlling factor of growth in the cylinder soils, and that the amounts applied were not too large to be properly utilized by the crops.

Comparing the relative influence of sodium nitrate, ammonium sulphate and dried blood (Series 8, 17 and 18) when used in equivalent amounts we note that the nitrate was (with one exception) superior to the ammonium sulphate and the latter superior to the dried blood. Similarly, when these materials were used in combination with the solid, leached (Series 14, 19 and 20), the nitrate was always superior to the ammonium sulphate and the latter always superior to the dried blood. A more accurate comparison of the returns from these substances will be afforded in the table showing the nitrogen yields, but in this place it may be noted that in so far as the corn crops are concerned the difference between the dried blood and ammonium sulphate is greater than that between the ammonium sulphate and sodium nitrate, no matter whether these materials were used alone or in combination with manure.

It now remains to note the influence of the lime applied in the spring of 1908 on the production of dry matter in the several soils. That the lime favored the growth of the crop is evident from the larger yields in the limed soils as shown in the last column of Table IV. In Series 1 the lime increased the yield of dry matter from 65.0 grams to 109.5 grams. It happens, however, that in this series the supply of available phosphorus is even smaller than that of available nitrogen, and we behold therefore the interesting action of lime in making available a larger supply of phosphorus. In the remaining series, nitrogen is the controlling factor, and the application of lime was indirectly equivalent to an application of nitrogenous materials. The lime corrected in most instances the existing acidity and encouraged bacterial growth and the decomposition of the organic matter.

We may note, particularly, the influence of the lime in Series 7, 8 and 18 where nitrate and dried blood were used. No manure has been employed in these series; their crop residues have been smaller and the bacterial activities less satisfactory than in other series where both crop and manure residues were of considerable significance. For this reason, the addition of lime stimulated decay processes to a relatively greater extent in Series 7, 8 and 18. In Series 17 the acid conditions were even more pronounced than those in Series 18. There is reason to believe, however, that the lime added was not adequate to fully correct this acidity, hence the increased yield in Series 17 was relatively much smaller than that in Series 18. Furthermore, the dried blood left larger residues in the soil than were left by the ammonium sulphate, hence the lime unlocked a larger reserve in Series 18.

TABLE V. THE AVERAGE PROPORTION OF NITROGEN IN THE DRY MATTER.

Series.	1898, %.	1903, %.	1908, %.	1908, A's, %	1908, B's and C's, %.
1	0.810	1.172	0.729	0.857	0.692
2	0.642	0.619	0.538	0.547	0.534
3	0.729	0.650	0.545	0.558	0.539
4	0.659	0.552	0.459	0.441	0.467
5	0.667	0.651	0.526	0.528	0.522
6	0.641	0.636	0.511	0.482	0.544
7	0.737	0.632	0.489	0.496	0.488
8	0.646	0.673	0.478	0.506	0.467
9	0.665	0.675	0.516	0.533	0.509
10	0.704	0.583	0.472	0.455	0.481
11	0.706	0.575	0.499	0.499	0.499
12	0.792	0.575	0.485	0.452	0.499
13	0.673	0.564	0.508	0.506	0.511
14	0.705	0.501	0.455	0.460	0.453
15	0.690	0.596	0.520	0.521	0.520
16	0.836	0.604	0.481	0.477	0.483
17	0.697	0.511	0.492	0.542	0.472
18	0.732	0.582	0.585	0.597	0.580
19	0.726	0.512	0.550	0.565	0.544
20	0.677	0.545	0.584	0.563	0.592

The data concerning the relative amounts of nitrogen in the corn crops of the different seasons and from the different series bring to light facts of considerable significance. It is shown in Table V that the proportion of nitrogen in the crops of Series 1 was much higher than that in the crops of any other series. In 1908, the dry matter of Series 1 contained 0.810 per cent. of nitrogen, and that of Series 6, 1.641 per cent. of nitrogen. In 1903, the dry matter of Series 1 was, relatively, even richer in nitrogen than it was in 1908. It contained 1.172 per cent. of nitrogen, or more than twice that present in the crops of some of the other series. In 1908, the proportionate amount of nitrogen in the dry matter of Series 1 was smaller than it was in 1903, but none the less much higher than that in the dry matter of the other series.

This abnormally high proportion of nitrogen may be readily attributed to the retarded growth of the plants occasioned by lack of available phosphoric acid. There was not enough of the latter for the production of a greater quantity of plant substance and the available nitrogen compounds taken up could not be utilized to better advantage. Under actual field conditions similar results are undoubtedly produced by lack of available phosphoric acid or of available potash. The nitrogen is not utilized economically in so far as the plant substance is made to carry a proportion much above the average.

But apart from the soils of Series 1 where phosphorus rather than nitrogen has been the controlling

element, we note appreciable differences in the proportionate content of nitrogen in the dry matter. We may observe, for instance, that in Series 3 the dry matter had a relatively higher proportion of nitrogen than in Series 4, notwithstanding the fact that the yield of dry matter and, as we shall see later, also of total nitrogen was higher in Series 4. Otherwise stated a larger quantity of available nitrogen compounds in the soil need not necessarily increase the proportion of nitrogen in the crop. It is only when the store of available nitrogen compounds becomes very large that the plants take up more than they can utilize advantageously, and yield, in consequence, dry matter with an abnormally high proportion of nitrogen. On the other hand, applications of nitrogen judiciously made may increase the yields of dry matter not only directly, but also indirectly by encouraging a more economical utilization of the nitrogen derived from the soil itself.

A very striking corroboration of the fact that the character of the season, as well as soil conditions, may affect the proportion of nitrogen in the dry matter is furnished by the corn crops of the three seasons under consideration. We may see at a glance that the crop of 1898 was proportionally richer in nitrogen than the crop of 1903, and that the latter, in its turn, was richer than the crop of 1908. The only exceptions to be made here are those relating to the yields of Series 1, 17, 18, 19 and 20. In the case of Series 1, the utilization of the soil nitrogen was effected by lack of available phosphoric acid and in Series 17–20 by the gradually increasing acidity which was more pronounced here than it was in the remaining series. In the latter, however, the influence of the season, that is of the differences in precipitation, average temperatures, and sunlight directly affected the economy of utilization of the available nitrogen compounds, and led thus to variations in the ratio of nitrogenous to non-nitrogenous substances in the crop.

The influence of the lime applied in 1908 is made manifest in the crops of that season. By comparing the proportions of nitrogen in the crops of the unlimed soils 1A–20A with those in the crops of the limed soils 1B–20C we observe at once that the lime lowered in most instances the proportion of nitrogen in the dry matter. Now, as we shall see presently, the lime increased the yields of total nitrogen and acted, therefore, like a nitrogenous manure. We have seen, however, that, when applied within certain limits, nitrogenous manures tend to lower the proportion of nitrogen in the dry matter; hence the analogous action of lime may be readily explained.

The figures in the fourth and fifth columns of Table V show us, in the first place, that the soils of Series 9, 11, 13 and 15 whether limed or unlimed produced dry matter richer in nitrogen than that produced in Series 10, 12, 14 and 16. Since, however, the series last mentioned were supplied with double the amount of nitrate in addition to the manure employed, and yielded in consequence a greater amount of total nitrogen, it follows again that under certain conditions small applications of nitrate may favor, to a greater extent than large applications, the production of dry matter rich in nitrogen. It should be remembered at the same time, that these relations will not be maintained when the quantities of available nitrogen compounds present are large.

It happens, thus, that in a few of the series the applications of lime increased, rather than decreased, the proportion of nitrogen in the dry matter. We see this increase distinctly in Series 6, 10, 12, 16 and 20; that is, in series that had large manure or crop residues. We may note in this connection that in the corn crop of 1898, the amounts of available nitrogen compounds were so large that the larger applications of nitrate in Series 10, 12, 14 and 16 resulted in the production of dry matter richer in nitrogen than that produced with the aid of the smaller applications in Series 9, 11, 13 and 15.

TABLE VI. —THE AVERAGE YIELDS OF TOTAL NITROGEN.

Series.	1898. gms.	1903. gms.	1908. gms.	1908. A's. gms.	1908. B's and C's. gms.
1	1.740	0.832	0.691	0.557	0.758
2	1.870	0.991	0.887	0.820	0.921
3	2.450	1.352	1.335	1.249	1.378
4	3.060	1.817	1.589	1.499	1.634
5	2.580	1.534	1.358	1.246	1.414
6	2.540	1.595	1.347	1.224	1.408
7	2.430	1.244	1.084	0.932	1.160
8	2.480	1.533	1.466	1.300	1.549
9	2.410	1.905	1.687	1.535	1.762
10	2.790	2.256	1.793	1.742	1.818
11	3.390	2.069	2.340	2.085	2.467
12	3.990	2.492	2.391	2.074	2.549
13	2.830	1.601	1.586	1.497	1.676
14	3.180	2.045	1.892	1.743	1.966
15	2.610	1.811	1.588	1.542	1.610
16	3.250	2.271	1.973	1.841	2.039
17	2.600	1.464	1.339	1.295	1.360
18	2.360	1.312	1.276	1.086	1.371
19	3.120	2.041	1.891	1.791	1.941
20	2.590	1.892	1.740	1.397	1.912

Table V showed that there was a proportionate decrease in the nitrogen content of the dry matter from 1898 to 1903 and from 1903 to 1908. Table

VI shows that the decrease was absolute. Comparing columns 1, 2 and 4 of this table we find this decrease to have occurred in all but one instance. As was to be expected, the decrease was greatest between 1898 and 1903. It has been pointed out that the nitrogen yields of 1898 were abnormal because of the treatment of the soil incident to the installation of the experiment. Between 1903 and 1908 the decrease was not so great, yet quite appreciable.

In Series 1, the nitrogen yield of 1908 was less than a third of the yield of 1898. In Series 2, as well as in some of the other series, it was less than half. It seems, therefore, that notwithstanding the comparatively large applications of manure and fertilizer in a number of the series the ability of the soils to yield maximum amounts of nitrogen in the crops was not maintained. We should have expected this at least from Series 10, 12, 14 and 16 which have been receiving annual applications of manure at the rate of about 16 tons per acre and of nitrate of soda at the rate of 320 pounds per acre. For all that there has been a distinct falling off in the nitrogen yields even in these series.

As to the influence of the nitrogen treatment we find that the solid and liquid, fresh, furnished more nitrogen to the crops than was furnished by the solid, fresh. This is readily apparent in the yields of Series 3 and 4. On the other hand, the leached manures showed scarcely any difference. Moreover, there was but a slight difference between the yields from the solid, fresh and those from either of the leached manures. We may properly conclude, therefore, that the superiority of the solid and liquid, fresh, should be ascribed to the water-soluble amino compounds and their derivatives in the liquid portion.

Comparing the yields of nitrogen from nitrate, ammonium sulphate and dried blood, where these were used without manure we find the efficiency of these materials to have been in the order named. In 1898 the returns from these materials were 2.480 grams, 2.600 grams, and 2.360 grams, respectively. The corresponding figures in 1903 were 1.533 grams, 1.464 grams, and 1.312 grams, respectively, and in 1908, 1.300 grams, 1.295 grams, and 1.086 grams, respectively. It will be noted, therefore, that yields from Series 17 in 1898 furnished the only exception to the rule.

We find, similarly, that the yields from the double quantity of nitrate were invariably larger than those from the single quantity. This applies not only to the series where the nitrate was used alone, but also to those where it was used in combination with the different manures. A comparison of the yields in Series 9 and 10, 11 and 12, 13 and 14, 15 and 16 will show this invariably to have been the case. The combinations of nitrate and manure show, likewise, that the solid and liquid, fresh (Series 11 and 12), was in all cases superior to the solid manure, fresh.

It now remains to consider the influence of the lime applied in 1908. We may note, in the first place, that the limed soils furnished in all cases more nitrogen to the crop than was furnished by the unlimed soils. Even Series 1, where phosphorus is now the controlling element of growth, produced a larger crop of corn where lime was applied. In this case, however, the lime evidently helped to make available a larger amount of phosphoric acid, as well as of nitrogen. In Series 2, where only acid phosphate and muriate have been applied for eleven consecutive years, the more readily decomposable portion of the humus had been largely depleted, nevertheless, the lime hastened the decay of the inert residues and made possible a markedly larger yield of nitrogen in the crop.

In how far the lime affected the increased utilization of the manure and crop residues in the other series may be seen from the following table which shows the increase over the yields of nitrogen in Series 2.

TABLE VII.—INCREASED YIELDS OF NITROGEN OVER THE CHECK PLOT.

Series.	A's, gms	B's and C's, gms	Difference, gm.
3	0.362	0.491	0.129
4	0.612	0.747	0.135
5	0.359	0.527	0.168
6	0.337	0.521	0.184
7	0.045	0.273	0.228
8	0.413	0.662	0.249
9	0.648	0.875	0.227
10	0.855	0.931	0.076
11	1.198	1.580	0.382
12	1.187	1.662	0.475
13	0.592	0.789	0.197
14	0.856	1.079	0.223
15	0.655	0.723	0.068
16	0.954	1.152	0.198
17	0.408	0.473	0.065
18	0.199	0.484	0.285
19	0.904	1.054	0.150
20	0.510	1.025	0.515

The increase which may be attributed to the lime appears to be greater in the leached manure series (5 and 6) than in the fresh manure series (3 and 4). On the other hand, in series that had received applications of both manure and nitrate, the superiority of the leached manures is not as

apparent. In fact the greatest increase to be ascribed to the lime occurred in Series 11 and 12. The increase due to lime was but slight in Series 17 and 19 and very considerable in Series 18 and 20. The difference in question may be ascribed partly to the greater proportion of nitrogen residues in the dried blood series; and partly, also, to the strongly acid condition of the soils in Series 17 and 19; hence, to the insufficient amount of lime applied.

THE PROPORTION OF THE APPLIED NITROGEN RECOVERED IN THE CROPS.

The yields of nitrogen in Series 2 must be attributed entirely to the soil humus, since no applications of nitrogen have been made in this series. By assuming a similar yield from the soil humus of the other series, and by subtracting this yield from that actually secured we obtain the yield due to the nitrogenous material added. For instance in 1908, the average yield of nitrogen in Series 2 was 0.887 gram, and in Series 3, 1.335 grams. Subtracting the former quantity from the latter we obtain 0.448 gram of nitrogen as due to the 4 grams of solid, fresh, applied in Series 3. This increase divided by the amount applied gives us the proportion of the applied nitrogen recovered. The remaining calculations carried out in this manner furnish the necessary data for a table showing the recovery from the several nitrogenous materials employed in the present experiments. The relations in question are brought out in the following table:

TABLE VIII.—THE PROPORTION OF NITROGEN RECOVERED.

Series.	1898, %.	1903, %.	1908, %.	1908, A's, %.	1908 B's and C's, %.
3	7.44	9.00	11.20	10.72	11.42
4	22.04	20.70	17.55	16.97	17.82
5	16.80	13.70	11.77	10.65	12.32
6	22.36	15.10	11.50	10.10	12.17
7	69.58	25.00	25.26	14.36	30.64
8	44.38	35.00	37.35	30.97	40.51
9	9.64	19.10	16.74	14.96	17.59
10	10.11	22.80	16.32	16.61	16.16
11	24.62	22.60	30.40	26.46	32.34
12	30.28	27.10	27.10	22.60	29.33
13	11.56	12.80	22.01	14.16	25.92
14	19.07	19.10	18.11	16.63	18.83
15	19.76	17.20	14.67	15.10	14.41
16	20.14	23.10	19.57	18.40	20.14
17	44.24	34.90	27.90	29.32	27.10
18	42.36	20.70	24.78	16.94	28.66
19	21.77	18.80	17.86	17.10	18.15
20	16.55	16.30	15.31	10.36	17.79
Av.	25.15	20.72	20.30	17.36	21.74

As indicated by the figures in Table VIII the proportion of nitrogen recovered in the corn crops was not large. Taking the average recovery for all of the applications we find that 25.15 per cent. of the nitrogen applied was recovered in 1898, 20.72 per cent. in 1903, and 17.36 per cent. in 1908 (unlimed soils). The averages just given were secured by adding the figures in the corresponding column and dividing by 18. They are somewhat higher than the real averages which may be obtained by dividing the average increase by the average amount of nitrogen applied. It happens, thus, that of the various applications of nitrogen less than one-quarter was returned in the crops. Not the least interesting fact in this connection is the much higher recovery in the oats crop that followed the corn crops of 1898 and 1903. In spite of the shorter growing season these crops were apparently able to secure more nitrogen from the materials applied.

The data at hand show us also that the recovery from the solid and liquid, fresh, was greater than that from the other manures, a fact which may be readily explained from the composition of the several manures. We may note, likewise, that the returns from the single application of nitrate (Series 7) were smaller than those from the double application in 1903 and 1908. In fact the single application in 1908 showed a recovery of only 14.36 per cent. (unlimed soil) probably because of the increasing acidity of the soil. The double application of nitrate maintained its superiority over the single application even when it was used in combination with manure. With but one exception Series 10, 12, 14 and 16 showed a higher recovery than the corresponding Series 9, 11, 13 and 15.

The falling off in the recovery from the nitrogen applied was marked in Series 17 and 18. In the first of these the proportion recovered was decreased from 44.24 per cent. in 1898 to 29.32 per cent. in 1908, while in Series 18 it was decreased from 42.36 per cent. to 16.94 per cent. Moreover, the decrease was considerable even in the series where the ammonium sulphate and dried blood were used in combination with manure. Thus in Series 19 the recovery decreased from 21.77 per cent. to 17.10 per cent., and in Series 20 from 16.55 per cent. to 10.36 per cent.

The application of lime in 1908 enhanced the recovery in all but three of the series. Among the latter is included Series 17 where the application of lime was not sufficient to neutralize all of the acidity. Examining the increase due to lime somewhat more critically we note it to have been particularly marked in Series 7, 8 and 18 whose

soils receive no applications of manure. Similarly, in some of the series receiving both nitrate and manure the increase was comparatively large, namely, in Series 11, 12 and 13. To these may be added Series 20 receiving applications of solid, leached, and of dried blood.

It should be pointed out here that the figures in Table VIII were obtained by subtracting the average yield of Series 2 from that of each nitrogen-treated series, and dividing the difference by the amount of nitrogen applied. The figures thus secured represent the average recoveries. Where the unlimed and limed soils were considered separately, the yield of 2A was subtracted from the corresponding yields of 3A–20A, and the average yield of 2B and 2C from the corresponding yields of 3B–20C.

THE ACTUAL AND CALCULATED RECOVERIES OF NITROGEN.

It will be remembered that in some of the series, manure was used alone, that in other series nitrate, ammonium sulphate or dried blood was used alone, and that in other series still the two classes of nitrogenous substances were used in combination. Now, it has been shown that by subtracting the yield of Series 2 from that of any of the nitrogen-treated series the increase due to that particular treatment is obtained. Knowing, therefore, the increase due to manure on the one hand, and to nitrate on the other, we may calculate the increase that should occur when the two are used in combination. We have determined thus the actual and calculated recoveries for the several series as shown in the above table.

TABLE IX.—ACTUAL AND CALCULATED RECOVERIES.

		1898.			1903.			1908.		
Series.	Series.	Actual, per cent	Calculated, per cent.	Not recovered, per cent.	Actual, per cent.	Calculated, per cent.	Not recovered, per cent.	Actual, per cent.	Calculated, per cent.	Not recovered, per cent.
7 and 3 in....	9	9.64	16.26	6.62	19.1	11.6	...	16.74	13.49	....
8 and 3 in....	10	10.11	16.61	6.50	22.8	16.3	...	16.32	18.50	2.18
7 and 4 in....	11	24.62	28.16	3.54	22.6	21.4	...	30.40	18.81	....
8 and 4 in....	12	30.28	27.14	.....	27.1	24.7	..	27.10	23.08	....
7 and 5 in....	13	11.36	25.46	14.10	12.8	15.5	2.7	22.01	13.97	....
8 and 5 in....	14	19.07	24.55	5.48	19.1	19.7	0.6	18.11	18.92	0.81
7 and 6 in....	15	19.76	30.96	11.20	17.2	16.7	...	14.67	13.74	....
8 and 6 in....	16	20.14	29.34	9.20	23.1	20.6	...	19.57	18.72	....
17 and 5 in....	19	19.75	24.67	4.92	18.8	19.8	1.0	17.86	16.42	....
18 and 5 in....	20	15.85	22.41	6.56	16.3	15.7	...	15.31	15.44	0.13

The differences between the calculated and actual recoveries, as shown in Table IX, appear greatest in 1898. In that year the calculated recoveries exceeded the actual recoveries in all of the combination series except in Series 12. For instance, in Series 9 the calculated recovery was 16.26 per cent., and the actual recovery 9.64 per cent. In other words, out of a possible 16.26 per cent., 6.62 per cent. were not recovered. It might be concluded, therefore, from the results of 1898, that denitrification had taken place in the combination series; that is, a portion of the nitrate applied had been destroyed in the presence of the manure.

But when we come to examine the results for 1903 and 1908 we find no such evidence of denitrification. In these years the actual recoveries exceeded the calculated recoveries in nearly all of the combination series, while in the few exceptions the calculated recoveries exceeded the actual recoveries but slightly. The apparent denitrification in 1898 must be attributed, therefore, to the inability of the plants to utilize thoroughly the comparatively large amounts of available nitrogen compounds in the combination series. Moreover, if the differences noted in 1898 were really due to denitrification they should have been greater in 1903 and greater still in 1908 on account of the cumulative effect of the annual applications of cow manure. As a matter of fact there was no such increasing apparent effect of denitrification. It may be concluded, in view of the data just presented, that under ordinary conditions of field practice denitrification is not a phenomenon of economic importance. In market gardening and in greenhouse work the conditions are different, and the significance of denitrification may be greater. However, it would be beyond the scope of the present paper to discuss those other conditions here.

THE ACTUAL AND CALCULATED RECOVERIES FROM THE UNLIMED AND LIMED SOILS IN 1908.

As supplementary to the data of Table IX, it would be proper to consider here the corresponding relations in the unlimed and limed soils of 1908. These relations are shown in the following table:

Table X Actual and Calculated Recoveries, 1908.

		Unlimed.			Limed.		
Series.	Series	Actual, %.	Calculated, %.	Not recovered, %.	Actual %.	Calculated, %.	Not recovered %.
7 & 3 in	9–	14.96	11.32	....	17.59	14.56	....
8 & 3 in	10–	16.61	16.38	. .	16.16	19.55	3.39
7 & 4 in	11–	26.46	16.55		32.34	19.92	....
8 & 4 in	12–	22.60	20.88		29.33	24.16	....
7 & 5 in	13–	14.16	11.25		25.92	15.31	...
8 & 5 in	14–	16.63	16.32		18.83	20.20	1.37
7 & 6 in	15–	15.10	10.79	.	14.41	15.18	0.77
8 & 6 in	16–	18.40	15.93	.	20.14	20.10	....
17 & 5 in	19–	17.10	16.03	.	18.15	16.58	....
18 & 5 in	20–	10.36	12.42	2.06	17.79	16.70	....

As is shown in the above table, the actual recovery exceeded the calculated recoveries in 9 out of 10 cases in the unlimed soils, and in 7 out of 10 cases in the limed soils. This furnishes us an apparent indication of denitrification in the limed soils, the more so since in Series 9 the actual recovery exceeds the calculated recovery by more than 3 per cent., while in Series 10 the calculated recovery exceeds the actual recovery by nearly as much. Similarly, in the other odd series where 5 grams of nitrate were applied the differences between the actual and calculated recoveries are much greater than they are in the corresponding even series where 10 grams of nitrate were used with the manure. It appears, therefore, that larger losses occurred where larger amounts of nitrate were used and that these losses might have been due to denitrification. It might be assumed, moreover, that the lime favored denitrification, since the corresponding differences are not so marked in the unlimed soils. However, the evidence at hand is inadequate as a proof of denitrification. It is more likely that the apparent losses of nitrogen were caused by the transformation of available into inert compounds. Indeed the comparatively low recoveries of the nitrogen applied for the corn crops seem to point strongly to the accuracy of this conjecture. Now, since lime encourages the rapid multiplication of soil bacteria, it is not at all improbable that more nitrate was thus transformed in the limed than in the unlimed soils. Information more definite in character than that already at hand can only be secured by means of carefully performed soil analyses.

THE RELATIVE AVAILABILITY OF THE NITROGENOUS MATERIALS.

By taking the returns from the nitrate nitrogen as 100 and by calculating the returns from the other materials on this basis we may secure a statement as to the *relative availability* of these materials. Properly tabulated figures representing relative availabilities may be quite helpful in the study of the comparative values of nitrogenous substances used as manures. The following table shows the relative availabilities of the several nitrogenous materials employed in the cylinder experiments for the corn crops of 1898, 1903 and 1908.

The data of Table XI bring out in a somewhat more concrete form facts already considered in preceding pages. We note the comparatively high availability of the ammonium sulphate, and of the solid and liquid, fresh, among the manures. We note, also, that in the limed soils the relative availability of the ammonium sulphate and of the several manures is diminished. Otherwise expressed, the sodium nitrate series were favored to a greater extent than the other series (Series 18 excepted) by the application of lime. It appears, further, that ammonium sulphate is a relatively better source of nitrogen for corn than it is for other crops. This may be ascertained by examining the data in the last column of Table XI. The relative availabilities given there represent the average for the ten-year period 1898–1907. The ammonium sulphate is shown there to have a relative availability of 69.7 as against 99.5, 99.8 and 94.7 (unlimed soils) for the corn crops of 1898, 1903, and 1908, respectively. The differences appear even more pronounced when the relative availabilities for 1898 and 1903 are excluded from the general average for the ten-year period.

Table XI.—Relative Availabilities

	1898.	1903.	1908.	1908, A's.	1908, B's and C's.	Average for all crops, 1898–1907.
Sodium nitrate	100.00	100.0	100.0	100.0	100.0	100.0
Ammonium sulphate	99.50	99.8	74.7	94.7	66.9	69.7
Dried blood	95.40	59.2	66.3	54.7	70.7	64.4
Solid manure, fresh	16.76	25.7	30.0	34.6	28.2	35.9
Solid and liquid, fresh	49.06	59.2	47.0	54.8	44.0	53.0
Solid manure, leached	37.86	39.2	31.5	34.4	30.4	38.9
Solid and liquid, leached	50.38	43.2	30.8	32.6	30.0	43.1

POTASH TESTS IN MIXED FERTILIZERS.[1]

By J. E. BRECKENRIDGE.

Received January 15, 1909.

The conditions which the fertilizer chemist has to meet are hard to realize, unless one has had personal experience, as such.

Especially is this true with regard to potash tests. On the one hand, the official methods, as outlined by the Association of Official Agricultural Chemists, must be followed and on the other hand we must satisfy the superintendents in finding the potash which they put into the goods.

A brief account of the work of the Association of Official Agricultural Chemists during recent years, as reported in their proceedings, will give us some very interesting and profitable information.

In 1896 Messrs. Scoville, Peter and Curtis revealed the fact that it was necessary to use 300 cc. of water for making potash solution in order to prevent potash from being occluded in porous materials. Experiments were tried on filter paper and chamois skin and when small amounts of water were added to potash and these porous materials, the loss was 0.49 per cent. on 3.11 per cent. in case of filter paper and 0.40 per cent. in case of chamois skin. This loss was reduced to 0.03 per cent. by using 300 cc. of water and then making solution to 500 cc. and proceeding as usual. It was also found that when 10 grams calcium phosphate were treated with 10 cc. dilute sulphuric acid, boiled for one-half hour, known amount of muriate of potash and water to 300 cc. added, then ammonia and ammonium oxalate and solution made to 503.5 cc., the 3.5 cc. accounting for the precipitate, that there was a loss of potash of 0.15 per cent. on 3.11 per cent. and 0.20 per cent. on 6.22 per cent.

Conclusion.—Calcium phosphate precipitated carries down or occludes more potash than organic materials such as filter paper or chamois skin.

The report for 1900 gives results of official method on acid phosphate and muriate mixture, showing the work of eleven experimenters. They found 6.12 per cent. K_2O on 6.37 per cent. theory, a loss of 0.25 per cent.

They found 3.07 per cent. K_2O on 3.23 per cent. theory, a loss of 0.16 per cent.

Conclusion.—Low results on potash in Acid Phosphate and Potash mixtures, but lack of time prevented further work.

1901.—At suggestion of Mr. Carpenter, Mr. Hare, referee, took up work of finding lost potash as experienced by official method.

Results showed loss of 0.23 per cent. on 3.55 per cent. theory.

Ammonium chlorid was tried as solvent for potash but gave only 0.07 per cent. increase in K_2O.

Conclusion.—Further investigation into loss of potash by official method.

1902.—Mr. McDonnell, referee, reported loss of 0.40 per cent. K_2O on 5.46 theory; when 10 per cent. sulfate of potash and 90 per cent. acid phosphate were mixed together, about a 7 per cent. loss.

On a mixture of 25 per cent. kainit, 40 per cent. acid phosphate, 20 per cent. blood and 15 per cent. fish, there was a loss of 0.20 per cent. on 3.11 per cent. theory, or about 7 per cent.

Conclusion.—Further study of loss of potash by official method.

1903.—Mr. Carpenter, as referee, introduced the method of adding 5 cc. HCl to 300 cc. water for making solution, adding soda in slight excess, then ammonium oxalate and proceeding as in the official method.

Results showed 4.56 per cent. on 4.55 per cent. theory on a sample of acid phosphate and muriate. Sample was also dissolved in regular citrate solution as used for insoluble phosphoric acid and only 0.10 per cent. was found insoluble in citrate solution as an average for ten workers, showing the potash found was at least available.

Mr. Carpenter also tried 10 grams of sample of acid phosphate and potash boiled with 300 cc. water 1/2 hour, added ammonia and ammonium oxalate and filtered. Boiled residue with same amount of water, filtered and washed. Acid solution of resulting residue showed 0.30 per cent. K_2O. 5 grams gave similar results.

Conclusion.—Further investigation.

1904.—Under Mr. Carpenter, as referee, two samples were tried by the official method and Carpenter or modified method.

Sample No. 1. Acid phos. and muriate. Theory 4.31 per cent. K_2O.

Official method, 19 workers, average 0.41 per cent. low.

Carpenter method, 19 workers, average 0.08 per cent. low.

Sample No. 2. Acid phos., animal tankage and muriate. Theory, 4.31 per cent. K_2O.

Official method, average 0.25 per cent low.

Carpenter method, average 0.03 per cent. high.

[1] Read at Meeting of American Chemical Society Dec. 31, 1908, Baltimore, Md.

We notice here that loss in acid phosphate and potash mixture is more than in acid phosphate, potash and tankage. This would seem to prove that the loss is caused by the acid phosphate and not increased by tankage as an absorbent material.

Mr. Carpenter recommended the adoption of the modified method, but it was decided to lay it over until 1905.

1905.—Under G. S. Fraps potash work was done on three samples.

No. 1 Sample.

Acid phosphate and potash. Theory 3.34%.

Official method:	Highest test	3.37%
	Lowest test	2.92%
	Difference	0.45%
Average of all (6) 3.08%, loss		0.26%
Modified method:	Highest	3.62%
	Lowest	3.17%
	Difference	0.45%
Average of all (6) 3.28%, loss		0.06%

No. 2 Sample.

Blood, acid phosphate and potash. Theory 3.37% K_2O.

Official method:	Highest	3.17%
	Lowest	2.93%
	Difference	0.24%
Average 3.05%; loss		0.32%
Modified method:	Highest	3.42%
	Lowest	3.16%
	Difference	0.26%
Average 3.27%; loss		0.10%

No. 3 Sample.

Cottonseed meal, acid phosphate and potash. Theory 3.80%.

Official method:	Highest	3.69%
	Lowest	3.18%
	Difference	0.51%
Average of all 3.52%; loss		0.28%
Modified method:	Highest	3.81%
	Lowest	3.62%
	Difference	0.19%
Average of all 3.70%; loss		0.10%

Again as in previous years we notice no apparent loss in complete goods over that in acid phosphate and potash. The acid phosphate seems to be the cause of the loss.

The referee reported that "we must conclude that the modified method gives results more nearly correct than does the official method."

The modified method was tried on some silicates with these results:

Feldspar	0.08% K_2O
Microline	0.08%
Leucite	0.30%
Apophyllite	0.27%
Muscovite 1.31 1.34 by official method	0.91%

(From these results we see there is no danger of the modified method dissolving much more insoluble potash than the official method.) State fertilizer laws were discussed and it was found 21 states required "potash soluble in water" or "distilled water."

"Law being made to exclude insoluble silicates, it might be argued that a method which does not include such potash and gives credit for the water-soluble potash placed in fertilizer, could be used."

Much discussion followed and when vote was taken the modified method was voted down.

1906 and *1907* added nothing of value as to finding lost potash, but the question of availability of potash was brought up by Messrs. Cushman & Bowker. No progress on available potash was made during these years nor in 1908, although it was decided in 1908 to appoint a special referee for available potash.

Conclusions which may be drawn from work of Association of Official Agricultural Chemists during the past few years are:

1. Loss of potash by official method in mixtures having acid phosphate and potash, this loss being in some cases as much as 7 per cent.

2. This loss does not seem to be increased by blood, tankage or cottonseed meal.

3. Laws of most of the states say "potash soluble in water," consequently no acid can be used for solution as in the modified or ignition methods.

4. In order to recover this potash and give the buyer a correct statement as to the potash contents, more work must be done trying to find method whereby water can still be used for solution and a chemical added, perhaps, to hold this lost potash or the laws must say in place of "potash soluble in water," "available potash" and leave it to the A. O. A. C. to devise method for determining available potash.

In view of the fact that potash tests on mixtures having acid phosphate and potash are low, as obtained by the official method, this having been the experience of the A. O. A. C. and also the experience at fertilizer factories, the following work has been done to locate this loss, if possible, and devise some method for finding this lost potash.

A sample of acid phosphate and muriate was mixed in laboratory and left on top of water oven for 24 hours.

This sample No. 1 was carefully prepared and well mixed and methods 1 to 10, inclusive, used, for analysis.

Method.—No. 1. Official method.

No. 2. Carpenter or modified method.

No. 3. Dissolved sample in 1 per cent. citric acid solution by heating on steam bath for 40 minutes, added NaOH in slight excess, then ammonium oxalate and proceeded as in official method.

No. 4. Same as No. 3, only used 2 per cent. citric acid for solution.

No. 5. Same as No. 3, only used ½ per cent. citric acid for solution.

No. 6. Same as No. 3, only used ammonia in place NaOH.

No. 7. 20 grams in 300 cc. water, heated 40 minutes on steam bath, cooled, made up to 500 cc., filtered. Took 50 cc. filtrate, put into 200 cc. flask, added water to 150 cc., heated to boiling, added ammonia and am. oxalate and proceeded as in official method, evaporating 50 cc. equivalent to ½ gram.

No. 8. Same as No. 7, only added 1 gram citric acid to the aliquot in 200 cc. flask before adding ammonia and ammonium oxalate.

No. 14. Digested residue on filter from No. 11 in 20 cc. conc. HCl, evaporated excess of HCl, washed into 200 cc. flask, made to about 150 cc., boiled, added ammonia and ammonium oxalate and proceeded as in official method, giving us the potash insoluble in water but soluble in conc. HCl.

From this series as shown in following table we find all methods for solution, except No. 10 (1 per cent. am.), give decided increases over official method on sample No. 1 especially the No. 7 method, 20 grams in 500 cc. filtered, etc. This would seem to indicate that the insoluble residue when left in flask and ammonium oxalate added had an influence on giving low potash tests.

The Carpenter and citric acid methods show well.

Sample No. 2. Acid phosphate and potash.

TABLE OF POTASH RESULTS.

Methods. / Samples.	1 Acid phos & mur.	2 Acid phos. & mur.	3 5–8–8	4 4–8–7	5 3–6–6	6 10–2	7 12–5	8 4–4–10	9 2–8–2	10 10–7	11 2–6–7	12 1–8–3	13 2–8–10	14 Cottonseed meal
1 Official	10.82	21.55	7.62	6.50	5.68	1.74	4.80	9.54	1.70	6.76	7.12	3.20	9.54	1.97
2 Carpenter	11.39	22.16	7.96	6.72	6.03	2.28	5.22	....	....	....	....	....	.....	....
3(*a*) Citric acid 1 per cent 40 min. digestion. NaOH	11.12	22.03	8.16	6.90	6.08	2.18	5.26	9.72	2.05	7.10	7.20	3.40	10.02	....
3(*b*) Citric acid 1 per cent. 36 hours digestion. NaOH	11.11	....	....	....	....	....	....	....	....	....	....	....	.....	....
4 Citric acid 2 per cent	11.18	....	....	....	....	....	....	....	....	....	....	....	.....	....
5 Citric acid one-half per cent	11 24	....	....	....	....	....	....	....	....	....	....	....	.....	....
6 Citric acid 1 per cent plus ammonia	11.18	....	8.16	6.93	....	....	....	....	....	....	....	....	.....	....
7 20 grams in 300 cc., etc.	11.20	22.18	7.91	6.96	5.70	1.60	4.65	9.32	1.56	7.02	6.64	3.18	9.54	....
8 Same as 7 plus citric acid	11 22	22.24	7.90	7.03	....	....	....	....	....	....	....	....	.....	....
9 10 per cent ammonia	11.24	....	....	....	5.58	....	....	....	....	....	....	....	.....	....
10 1 per cent. ammonia	10.69	....	8.14	7.04	5.78	....	....	....	....	....	....	....	.....	....
11 2 grams on filter plus citric acid	.....	....	8.08	....	6.04	1.66	4.78	....	1.60	....	6.92	....	10.04	....
12 2 grams on filter plus HCl	.....	....	....	....	6.02	1.78	4.78	....	1.56	....	....	....	10.16	....
13 2 grams on filter	.....	22.30	7.93	6.88	5.67	1.93	4.80	9 88	1.56	6.92	6.96	3.10	9.84	1.90
14 Insoluble on filter after washing	.....	0.06	....	....	0.02	0.81	0.54	....	0.48	....	0.08	0.50	.....	....
Difference between 1 and 3(*a*) in favor of 3(*a*)	0.30	0.48	0.54	0.40	0.40	0.44	0.46	0 18	0 35	0 34	0.08	0 20	0.48	....
Difference between No. 1 and 13 in favor of 13	.....	0.75	0.31	0 38	....	0.19	....	0 34	....	0.16	....	....	0.34	....

No. 9. Used 10 per cent. ammonia water for solution, heated 40 minutes on steam bath, added ammonium oxalate and then as in the official method.

No. 10. Used 1 per cent. ammonia water for solution, otherwise as in No. 9.

No. 11. Placed 2 grams on 11 cm. filter, washed with hot water, small portions at a time, into 200 cc. flask to about 175 cc., when there should be no chlorine or soluble sulfate left in residue, add to filtrate about 0.6 gram citric acid, heated to boiling, added ammonia and ammonium oxalate, then as in the official method, evaporating 50 cc. = ½ gram.

No. 12. Same as No. 11, only using 2 cc. HCl conc. in place of 0.6 gram citric acid.

No. 13. Same as No. 11, omitting 0.6 gram citric acid.

This was taken from stock in factory about three months old.

Results on this were:

Method No.	1...	21.50–21.60%	Difference. Official method
" "	2...	22.16%	+ 0.61% Carpenter method.
" "	3...	22.03%	+ 0.48% citric method
" "	7...	22.18%	+ 0.63% water-soluble method
" "	8...	22.24%	+ 0.69% water + citric method
" "	13...	22.30%	+ 0.75% 2 grams on filter

Here again we find the official method very low and No. 7 showing fine, Carpenter and citric also showing fine, 2 grams on filter showing best.

SAMPLE NO. 3 5—8—8 GOODS.

Method No.	1...	7.62%	Difference. Official method
" "	2...	7.96%	+ 0.34% Carpenter method
" "	3...	8.16%	+ 0.54% citric + soda
" "	6...	8.16%	+ 0.54% citric + ammonia
" "	7...	7.91%	+ 0.29% water-soluble
" "	8...	7.90%	+ 0.28% water-soluble + citric acid
" "	10...	8.14%	+ 0.52% 1% ammonia
" "	11...	8.08%	+ 0.46% 2 grams on filter + citric acid
" "	13...	7.93%	+ 0.31% 2 grams on filter

Again the official method is lowest, Carpenter and citric acid showing best, while 1 per cent. am. sol. method No. 10 shows fine. No. 7, No. 11 and No. 13 also show good gains.

SAMPLE NO. 4 4—8—7.

Method No.		Difference. Official method
Method No. 1...	6.50%	
" " 2...	6.72%	+ 0.22% Carpenter
" " 3...	6.90%	+ 0.40% citric
" " 6...	6.93%	+ 0.43% citric and ammonia
" " 7...	6.96%	+ 0.46% water-soluble
" " 8...	7.03%	+ 0.53% water-soluble + citric
" " 10...	7.04%	+ 0.54% 1% ammonia
" " 13...	6.88%	+ 0.38% 2 grams on filter

Again the official method shows lowest.

SAMPLE NO 5 3—6—6

Method No.		Difference
Method No. 1...	5.68%	
" " 2...	6.03%	+ 0.35%
" " 3...	6.08%	+ 0.40%
" " 7...	5.67%	— 0.01%
" " 9...	5.58%	— 0.10%
" " 10...	5.76%	+ 0.08%
" " 11...	6.04%	+ 0.36%
" " 12...	6.03%	+ 0.35%

Again methods Nos. 2, 3, 11 and 12 show decided gain while water solution and ammonium solution show low.

Sample No. 6 10—2.

SAMPLE NO. 6 10—2.

Method No.		Difference
Method No. 1...	1.74%	
" " 2...	2.28%	+ 0.54%
" " 3...	2.18%	+ 0.44%
" " 7...	1.60%	— 0.14%
" " 13...	1.93%	+ 0.19%

Again the Carpenter (No. 2) and citric (No. 3) methods show all right while it seems that No. 7 boiling with water and filtering lost a little. No. 13 shows well.

To try to locate where this loss occurred I made the following rests:

1. Acid phosphate + known amount of muriate in solution, then the official method showed a loss of 0.32 per cent. on 6.44 per cent.

2. Acid phosphate + water + NaOH in excess + am. oxalate, to precipitate all the lime before adding the potash, then added known amount of potash and proceeded as in official method gave still a loss of 0.27 per cent. and 0.21 per cent. on 6.44 per cent.

From this it would seem that the precipitate or insoluble material, or both, usually found in potash determinations, when solution has been made alkaline and am. oxalate added, takes up potash in some way and that it is not necessarily the precipitation that causes the loss. In fact our experience with method No. 7, filtering off the insoluble material, would seem to indicate that this insoluble material, calcium sulfate, silicates, dicalcic phosphate being a part of this insoluble, had the greatest influence on the lost potash. To further prove that the potash in usual acid phosphate and potash mixtures goes into solution readily and is lost in process, I took 2 grams of sample No. 2, acid phosphate and muriate testing 21.55 per cent. by the official method, placed on 11 cm. filter and washed with small portions of hot water to 175 cc. in 200 cc. flask, the washings no longer showing any chlorine, treated the residue with 20 cc. conc. HCl evaporating to 10 cc. washed into flask, boiled, added ammonia and ammonium oxalate and proceeded as in the official method (method No. 14) and found 0.06 per cent. K_2O. The water solution was analyzed by regular official method and showed 22.30 per cent. K_2O against 21.55 K_2O by the official method as usually carried out.

Sample No. 6 3—6—6 was analyzed for insoluble potash by washing on filter as on sample No. 2 and residue treated with conc. HCl and proceeded as before (method No. 14) and found 0.02 per cent.

In this sample we find the loss of potash in the process after removing the insoluble material probably due to the fact that there were more soluble salts, precipitated by the ammonia and ammonium oxalate, in this sample than in the samples No. 2 (5—8—8) and No. 3 (4—8—7). Methods No. 11 and No. 12 were tried on 3—6—6 and potash was found. The tabulated results will show the work done and the conclusions which can be drawn are:

1. That the official method gives low results.

2. That the potash found by the Carpenter and citric acid methods in samples No. 2 and No. 3 at least, is not insoluble potash, as shown by analyzing the insoluble residue after washing with hot water.

3. That filtering off the insoluble residue in some cases gives us higher results than the official method.

4. That while I believe the law should read "available potash" and so permit the use of HCl, or at least citric acid for solution, and recover the potash which was added as soluble but has probably formed zeolites as in samples No. 6, No. 7, No. 9 and No. 12, under the existing laws we are compelled to use water for solution. Satisfying this condition, method No. 7, 20 grams in 300 cc. water, etc., gives us a decided increase in potash over the official method on some samples and loss in others. Method No. 13 gives decided increase over method No. 7 on samples No. 8 and No. 13 with equally good results on others. Methods No. 11 and No.

12 give decided increases on samples No. 5 and No. 13 and will recover potash in many cases where the official method loses it.

LABORATORY AMERICAN AGRICULTURAL CHEMICAL CO.,
CARTERET, N. J.

CHEMISTRY OF FLESH.

(SEVENTH PAPER.)[1]

A PRELIMINARY STUDY OF THE EFFECT OF COLD STORAGE UPON BEEF AND POULTRY.

(FIRST COMMUNICATION.)

By A. D. EMMETT AND H. S. GRINDLEY.

Received March 10, 1909.

Up to the present time, the modern method of cold storage must be considered as the best means of preserving flesh from the standpoint of supplying a product which closely resembles the freshly killed meats. Further, it gives a safe and convenient medium wherein the physico-chemical changes of fresh meats can take place, as for example, rigor mortis which may occur almost immediately after death, later giving way to release rigor and thereby causing the flesh to become softer and more tender. Further in the continued hanging of the meats, they are supposed to become juicier, better in flavor and tenderer, or in the trade sense ripened and in prime condition for domestic use.

Naturally, the influence of the factor of time of keeping meats in cold storage is an interesting one, especially if we consider the transportation of meat products both at home and abroad. During a cold storage transit period of 22 days, the time required to go from Argentina to England, or of 40 days, the time to go from Australia to England, it would be instructive and perhaps of economic value to know more of the chemical changes which take place in the stored meats during transit. Whether cold storage influences the nutritive value of the food stuff, appreciably affecting its palatability or its comestibility, and if so an approximation as to the time when the changes take place would add to our present knowledge.

Another factor which is also of interest at the present time is the effect of cold storage upon frozen fowl, whether the drawn or undrawn bird is preserved equally well for the same length of time, and what are the differences, if any, in nutritive value in the two cases as compared with fresh fowl.

[1] H. S. Grindley, *Journ. of the Amer. Chem. Soc.*, xxvi, p. 1086 (1904); H. S. Grindley and A. D. Emmett, *Ibid.*, xxvii, p. 658 (1905); A. D. Emmett and H. S. Grindley, *Ibid.*, xxviii, p. 25 (1905); P. F. Trowbridge and H. S. Grindley, *Ibid.*, xxviii, p. 469 (1906); H. S. Grindley and H. S. Woods, *Journ. of Biol. Chem.*, **2**, p. 309 (1907); A. D. Emmett and H. S. Grindley, *Ibid.*, iii, p. 491 (1907).

With the object of making a chemical study of the influence of cold storage upon flesh, this investigation was undertaken. The present paper, which takes up the preliminary work in applying the improved methods of analyzing flesh,[1] to fresh and refrigerated products, deals as nearly as possible with the existing conditions first, as they relate to the storage of chilled or refrigerated beef for periods of time which may be counted as comparable to those required to ship and transport our products to their destination, and second to the storage of drawn and undrawn frozen fowl. In the meantime, W. D. Richardson[2] has applied the methods to a study of the deterioration and commercial preservation of flesh foods, and has proved that they are of real value in this connection. H. W. Wiley[3] has also used our improved methods for the analysis of flesh in his study of the effects of cold storage upon poultry.

HISTORICAL.

Among the investigators who have studied the effect of cold upon meats, may be mentioned Bouley[4] who in 1874 presented a paper before the French Academy of Science. He stated, in using Tellier's process of refrigeration, that at a temperature between +3° C. and —2° C. meat would keep indefinitely as far as putrescibility was concerned but not so from the standpoint of an edible food, for while the tenderness of the meat was increased with the time of storage a peculiar fatty odor developed toward the end of the second month which affected the flavor. Pogziale and a little later, in 1889, a commission appointed by the French minister of war confirmed Bouley's conclusions.

In 1892, Grassman[5] found in making a study of beef, pork, and mutton: that flesh kept in cold storage for 8 months at —2° to —4° C. did not deteriorate; that considered upon the dry basis the data indicated that there was no loss of nutritive material, this statement being based upon the following chemical determinations, moisture, total nitrogen, protein nitrogen by Stutzer's method, and fat; that refrigerated meats cook by roasting and boiling in a shorter time than do the fresh

[1] Grindley and Emmett, *Journ. Amer. Chem. Soc.*, xxvii, 658–678 (1905). Emmett and Grindley, *Ibid.*, xxviii, 25–63, (1906).

[2] *Journ. Amer. Chem. Soc.*, **30**, 1515–1564 (1908); THIS JOURNAL, **1**, 95–102.

[3] "A Preliminary Study of the Effects of Cold Storage on Eggs, Quail, and Chickens," *U. S. Department of Agriculture, Bur. of Chem., Bull.* 115 (1908).

[4] *Compt. rend.*, 79.

[5] *Landw. Jahrb.*, 21.

meats and that they are excellent in quality and tenderness; and that the loss of water by evaporation in storage was not an appreciable one. He concluded by recommending cold storage as a means of keeping meats.

In 1897, A. Gautier[1] published the results of a detailed study upon the differences between fresh and stored frozen mutton and beef. His fresh meats were obtained from steers and sheep which had been raised in France, while his frozen meats were procured, frozen, and stored in Argentina. The method of preparing these cold storage products was to subject the carcass of the animal to —15° C., until frozen to the center and then to keep it in a room at —5° C. In this case, the meats were held in storage for 5 to 6 months. Gautier took for his chemical investigation samples from the shoulder cut for the mutton and from the rump steak cut for the beef. In all cases the visible fat and tendon were removed before making the analyses. The author made a very thorough examination, determining: moisture, fatty matter by ether, soluble matter by cold water and by hot water (using the residue from the former in the latter case), myosine, myostrom, peptones, extractive matter, glycogen, reducing substances, gelatin, and indigestible matter. We quote in part from his own summary: Meats frozen and thus preserved for 5 to 6 months at —3° to —5° C. contain about 1 per cent. less of water than fresh butcher's meat. The assimilable albuminoids are a little more increased in the frozen than in the fresh meats, being 1.25 per cent. greater for mutton and 0.39 per cent. for beef. Frozen meats contain less gelatin than fresh meats. The weight and composition of the fatty matter are the same in both cases, but in the frozen meat the fat takes on a slight characteristic taste which allows it to be recognized after roasting. The extractive matters are not sensibly more abundant after storage, glycogen excepted. The peptonized parts of these meats have not appreciably varied. Boiled frozen meat is excellent and difficult to distinguish from fresh boiled meat. The cells of frozen meat remain unbroken on thawing. Frozen meats will remain untainted in the air for several days after being brought out of cold storage. By means of artificial digestion experiments with pepsin, there appears to be practically no difference in digestibility between fresh and frozen meats.

[1] *Rev. d. hyg.*, 19.

In 1901, C. Mai[1] claimed that by proper cold storage treatment putrefactive changes could be prevented, but that the action of ferments or enzymes would still continue to some extent and either directly or indirectly cause the changes which take place in the so-called ripening of meats.

Two years later, in 1903, M. Müller[2] emphasized in a discussion upon the ripening of meat: that besides a temperature of 0° C., the dryness of the air had a great deal to do in preventing the decay of such products. Under these conditions, the putrefying bacteria did not act, but the ferments or enzymes gradually made the meat more tender, juicy, and better in flavor. That the ripening of flesh which takes place throughout the entire mass and is not due in any sense to bacteria, is accompanied by a slow increase in acidity, while, on the other hand, decay of animal matter which is due to bacteria, produces an increase in alkalinity by the splitting off of ammonia. That the odor of ripened meat which is often taken by the inexperienced as indicating putrescibility is an entirely distinct one. That meats which have been ripened for roasting to the extent which the English fancy, will not do for boiling since they impart to the broth a disagreeable flavor. Finally, that broths from ripened meats are higher in extractives than those from fresh meats.

In 1905, Brittels,[3] in a paper upon Ship Refrigeration read before the Cold Storage and Ice Association of Great Britain, maintained that chilled meats could be carried longer than 25 days, as was then considered to be the limit for preservation. He added that at times meats from Australasia were on board as long as 40 days and yet when received were in perfectly satisfactory condition. It should be mentioned that Australasian chilled meats are slightly frozen and kept at about 29.5° F., and hence they do not compare with our chilled meats which are not frozen and are held in cold storage at approximately 33° F.

S. Rideal[4] made a report, late in 1906, of a chemical investigation which he had carried on for W. Weddels and Company of England. It contained data relating to the differences between Australian cold storage meats, both the chilled and frozen, and English and Welsh fresh meats. The beef, lamb, and mutton samples which he used were procured

[1] *Zeit. u. Nahr. Gens.*, 4.
[2] *Arch. f. Hyg.*, 47.
[3] *Cold Storage and Ice Trade Journal*, Vol 15, No. 6, June, 1906, p. 22.
[4] Cold Storage, England.

in the open market, but a fairly good descriptive history of each was obtained. Of the imported Australian meats, the chilled beef was from a bullock 8 months old. It was kept in storage at 29.5° F. during the voyage of 31 days. The frozen beef was from a River Plate ox about three years old, and was held in storage at 20° F. during the transit of 31 days. No data were given as to how long these animals had been slaughtered before shipment. The leg cuts, "Champion" brand, of frozen lamb and mutton, which were used, were held in storage two months and during shipping were kept at about 20° F. The domestic fresh beef was obtained from a Norfolk steer freshly slaughtered. The fresh lamb meat was of the Welsh-Raynor breed, and the mutton of the Leicester breed. In making the comparative tests in studying the differences in nutritive value and digestibility of the fresh, chilled, and frozen meats, the author procured for the beef the shin cut and two pounds of steak, and for the lamb and mutton, the leg cut. The percentage of lean, bone, and excessive fat were determined. The lean of the beef shin was analyzed chemically for moisture, fat, and total nitrogen. Portions were also taken and boiled six hours with water and the resulting extracts, which the writer designated as beef tea, were analyzed for mineral matter, fat, total nitrogen, and total solids. The lean of the beefsteak was examined as to the ease of digestibility with pepsin and hydrochloric acid. In the case of the leg of lamb and mutton, the meats were roasted in the usual manner, without removing the bone. The percentage loss in cooking and the amount of drippings were ascertained. The lean of the cooked meats was analyzed chemically for moisture, fat, and total nitrogen, and also as to differences in digestibility. The author, who had done some work in 1896 upon fresh and frozen domestic meats, concluded from this study, which confirmed the earlier one, that "no incipient decomposition or hydrolysis takes place under cold storage," and that the differences in nutritive value and digestibility of fresh, chilled, and frozen beef, lamb, and mutton were too slight to be of any economic importance.

In this same year, following the agitation regarding the packing houses of United States, the question relating to the proper preservation of food products qy cold storage was brought before Congress. As a result, it authorized that a "bacteriological-chemical study of the effect of cold storage upon the wholesomeness of food products" be made, and that special stress be put upon the chemical phase of the work. Among the first things to be taken up was the influence of cold storage upon flesh and in particular, the preservation of drawn and undrawn fowl. About this time H. S. Grindley made a report[1] to the Chicago City Council upon some work that had been done in this laboratory upon the differences between fresh and undrawn frozen fowl. The chemical data relating thereto are included in this paper. He stated that as far as could be found in the literature nothing had been done up to that time to prove scientifically: "First, that even slight decomposition takes place in the entrails of undrawn fowl during refrigeration; second, that the contents of the entrails infiltrate, diffuse, or by osmosis pass into the flesh; third, that refrigerated poultry, drawn or undrawn, decomposes more readily or more quickly than does fresh poultry." In making some practical tests for this report upon undrawn fowl which had been held in cold storage for two seasons, from September 16, 1904, to October 16, 1906, it was noted: that the general appearance of the undrawn refrigerated birds was not markedly different from the fresh birds; that the odor and appearance of the entrails were the same in both cases; that the refrigerated fowl, cooked by roasting and boiling, were exceedingly tender; that the roasted refrigerated fowl before adding any seasoning or condiments had a characteristic flavor which was not due to putrefaction but perhaps, as Müller[2] states, to the ripening of meats; that the fresh and refrigerated fowl cooked by the ordinary household methods were eaten and relished by two families who did not know anything of their previous cold storage; that no injurious effects resulted in the eating of these meats, and that undrawn fowl after removal from cold storage kept as long in an ordinary house refrigerator as did sound fresh chicken.

Early in 1906, J. D. Bird,[3] of Washington, D. C., made a practical test with drawn and undrawn turkeys. He hung the fowl, during the month of February, in the open air and found that at the end of the first week the undrawn turkey was perfectly sound while the drawn one showed distinct signs of decay.

E. M. Eckard, Commissioner of Health of Peoria, Illinois, made a bacteriological study of drawn and

[1] *Ice and Refrigeration*, **31** (1906).
[2] *Loc. cit.*
[3] *Ice and Refrigeration*, **32**, 1 (1907).

undrawn cold storage fowl. His results which were published[1] in 1907 were based upon samples procured in the open market, and nothing was known concerning the condition of the chickens before they were placed in cold storage. His conclusions were very decidedly in favor of the drawn fowl as compared with the undrawn.

Early in 1907, C. Harrington,[2] Secretary of the Massachusetts State Board of Health, made a preliminary report to the state legislature upon an extended investigation of the question of the changes taking place by cold storing drawn and undrawn fowl. In 1908, the final report[3] of the investigation was made and presented by W. F. Boos under the title of the "Chemical Examination of Drawn and Undrawn Poultry Kept in Cold Storage." The temperature of the storage room was maintained at about 0° F. Both chicken and duck were examined in the study. The problem resolved itself into the following questions: (*a*) Will the flesh of drawn or undrawn fowl undergo chemical change during cold storage? (*b*) Will drawn or undrawn fowl, after removal from cold storage, decompose with equal rapidity? (*c*) How will sterile drawn fowl compare with ordinary drawn and undrawn fowl as to their respective keeping qualities? The conclusions were: (*a*) That no chemical changes take place in cold storage in either drawn or undrawn poultry. This was determined by the fact that no ptomaines were found in using both Brieger's, and Baumann and von Udranszky's methods, and by the fact that when extracts of the flesh, prepared by using alcohol, and then taking up the evaporated residue with water, were injected intravenously into rabbits, no reaction was obtained. (*b*) That the undrawn fowl, when removed from cold storage, thawed in the open air, and kept at 68° F. for six days, showed less tendency to break down than did the drawn birds under exactly the same conditions. (*c*) That comparing the properly drawn, the ordinary drawn and the undrawn fowl when prepared fresh and left to hang at 68° F., the first showed the best keeping qualities, the second the next best, and the third the poorest. For the first 24 hours, the undrawn fowl kept equally as well as those properly drawn. (*d*) That the best means of preparing fowl for storage is to first draw them but properly, adding that "ordinary drawing is worse by far than no drawing at all."

[1] *Chicago Clinic*, **20**, 1.

[2] New York Produce Review and American Creamery 23-25 (1907).

[3] Thirty ninth Annual Report of the State Board of Health of Massachusetts.

H. A. Higley,[1] of the Brooklyn Diagnosis and Research Laboratory, prepared a detailed report as to the differences between fresh and refrigerated, drawn and undrawn fowl. Basing his conclusions upon established bacteriological facts, he found that "the edible portions of healthy, dead, undrawn poultry and game do not contain any bacteria, toxines, or ptomaines that are harmful when eaten by man so long as such poultry is kept free from putrefaction; that poultry that goes into cold storage in good bacterial condition comes out in exactly the same condition that it went in, so long as the temperature of the poultry is kept low enough (5° C., or below) to prevent the growth of putrefactive bacteria, and finally that the longer poultry remains frozen, the less bacteria does it contain."

In January, 1908, Wiley and associates[2] made a preliminary report upon an investigation which was being carried out at Washington, on the effect of cold storage upon eggs, quail and chickens. The bulletin[3] giving the detailed results of this work, was issued in November. In the case of the eggs, a bacteriological, microscopical and chemical examination was made. The first showed that at the end of three months, the whites and yolks were still separate but at the end of six months, they were more or less intermixed, the limiting membrane having been dissolved by the bacteria. The microscopical study indicated that at the end of 3½- and 6-month periods, the eggs were not unlike the fresh, but that at the end of 12½ months, the yolks of the cold storage product were flattened and contained rosette crystals. The chemical examination showed: That the cold storage eggs lost, during a period of one year, 10 per cent. of their weight, due chiefly to water; that the amount of coagulable protein and the lecithin phosphorus in samples, which were boiled, was less; that the proteose and peptone nitrogen increased, and that the amido constituents decreased.

In taking up the study of fowl, the work was divided somewhat: First, a preliminary investigation with quail and chicken, under known conditions as to cold storage, was undertaken in which organoleptic tests and bacteriological examinations were made, and second, a comparison of market cold storage chicken was undertaken upon a histological, bacteriological and chemical basis. In the former, drawn and undrawn birds were used. From the organoleptic tests, there seemed to be no

[1] *The National Provisioner*, **36**, 13.

[2] *Science*, **27**, p. 295 (1908).

[3] *U. S. Department Agr., Bur. Chem., Bull.* **115**.

marked distinctive points between the two. Comparing them with fresh samples, there was no apparent difference at the end of six weeks; however, after a period of three months or longer, the stored fowl showed a perceptible difference in the uncooked condition and in some cases in the cooked. The bacteriological examination gave positive evidence of bacterial growth during the storage period. The reduced temperature retarded their growth, but it did not destroy the organisms—a fact which Pennington[1] also found in the case of milk.

In the study of the market cold storage chickens, the samples were compared with fresh fowl. The previous history of the birds was not known. In the chemical work, the light and dark meats were each analyzed. A special study was made of the fat, the usual determinations being followed out. For the lean meat, the method, as published from this laboratory,[2] was used with some modifications. The conclusions, which were of a tentative nature, were: (*a*) The histological examination of the muscle of the stored and unstored fowl showed distinct and progressive changes in the structure of the fibre. (*b*) The bacteriological study gave evidence of the presence of an appreciable number of bacteria in the edible stored flesh but none in the fresh samples. (*c*) The chemical analysis indicated only slight variations for the different nitrogenous constituents but marked ones for the fat.

At the same time that Wiley and associates made their preliminary report, Richardson read a paper[3] on "The Criteria of the Deterioration of Flesh Foods." He used, in general, the methods of this laboratory with further improvements. Special emphasis was laid upon the value of the determination of ammoniacal nitrogen. Later Richardson and Scherubel[4] published an elaborate investigation upon experiments with samples of frozen beef knuckle kept at —9 to —12° C. Histological, bacteriological, and chemical studies were made. In the chemical work, the authors reported, in addition to the determinations made in our study, those for the ammoniacal nitrogen, acidity and sulphur. The histological data showed: That the physical changes in frozen meats were due either to the evaporation of the water, or to the pressure produced by expansion in the freezing of the water; that the formed ice which was outside of the cell, might produce abrasion of the cell wall depending, as Gautier[1] also stated, upon the rapidity of the freezing and the subsequent thawing, and that the solidifying point does not occur at any specific temperature but that it depends upon the soluble solids. From the bacteriological examination, it was found that in the freezing the bacteria became surrounded by solid barriers of ice through which they could not penetrate and hence they would cease to grow. In the chemical study, a comparison of the composition of the frozen sample was made with that of the fresh meat. There appeared to be no general tendency for the ammoniacal, the coagulable or the albumose nitrogen to increase or decrease and hence chemically the products of bacterial growth, if there were any, were inappreciable. The authors concluded from their results that frozen meats can be kept in cold storage under proper conditions for a period of 554 days or perhaps longer.

In a second paper,[2] Richardson and Scherubel have made a study of the preservation of meats stored at temperatures of 2 to 4° C., that is, above the freezing point. The same chemical methods were used here as in the preceding two studies; however, the data for the phosphorus and sulphur are not reported. Tests were made to ascertain whether the chemical methods would detect any changes resulting from known bacterial decomposition of meat. In the first experiment, samples of chopped beef knuckle were prepared, and to the same, 1 cc. of a putrefying meat infusion was added. These tests were kept for definite periods of time at room temperature. It was found that the total nitrogen, the meat base nitrogen, the coagulable nitrogen, the albumose nitrogen, the ammoniacal nitrogen, and the total solids all increased up to and including the ninth day. The total nitrogen and the meat base nitrogen showed a general increase throughout, while the albumose and coagulable nitrogen increased regularly at first, but later began to decrease, yet always remaining higher than at the start. The total acidity determinations were of no definite value. In the second test, chopped meat was again used and in some cases preservatives were added. The samples were kept in Mason jars at 2 to 4° C. The authors state that these experiments were not very satisfactory but, in general, they seemed to show that the added preservatives assisted in arresting the bacterial

[1] *Journ. Biol. Chem.*, **4**, 353 (1908).
[2] *Loc. cit.*
[3] *Science*, **27**, 687 (1908).
[4] *Journ. Amer. Chem. Soc.*, **30**, 1515 (1908).

[1] *Loc. cit.*
[2] THIS JOURNAL, **1**, p. 95 (1909).

action. The low temperature, however, was the chief agent. In a third test, cuts of beef knuckle were used. They were held in cold storage at 2 to 4° C. for varying lengths of time. It was found on the 31st day, and thereafter the samples were covered with a slimy layer. The analysis of the entire cut then showed the ammoniacal nitrogen to be twice as high as in the case of the sample for the seventh, fourteenth, and twenty-first days, and it also showed the albumose nitrogen to be about 30 per cent. higher. Analyses of samples on the thirty-ninth, forty-sixth, and fifty-third days were about the same as those for the thirty-first day. On and after the sixty-fifth day, there was a marked increase in the total, the coagulable, the albumose, and the ammoniacal nitrogens and in the total solids. In a fourth test, pieces of knuckle which had begun to decompose on keeping at 2 to 4° C. were transferred on the fifty-fourth day to a room whose temperature was —9 to —12° C. It was found that the reduced temperature arrested the bacterial decomposition.

From the above historical review, it is evident: first, that up to within the last two and a half years, comparatively little has been done outside of Gautier's work in making an extensive chemical study of the differences between fresh and cold storage flesh; second, that in all the cases reported, excepting those of Wiley, Richardson and Scherubel, and Grindley, either the conditions as to the temperature of the cooling room and the methods of preparing the meats for storage did not correspond with those in common usage in United States at present, or else, in the most comparable cases the chemical constituents determined and reported were quite few; third, that the tests in these cases, again excepting Wiley, Richardson and Scherubel, and Grindley, were made on the one hand, with chilled or frozen meats and on the other, with those used either soon after slaughtering or after hanging in the air for 30 to 60 hours at a temperature of approximately 9° C. and not in the strict sense of the word with meats which had been properly cold stored immediately after killing and then examined at different periods of time; fourth, that practically nothing has been reported, outside of Grindley's work, in making a chemical study in comparing the composition and nutritive value of fresh fowl with drawn and undrawn frozen fowl; and finally, that no one, as far as could be discerned, has published any results where the fresh, refrigerated, or frozen meats were all procured from the same animal, the same breed of animals, or from animals reared in the same locality, and hence as far as our present knowledge shows us, it might be assumed that the differences reported could have been still less, more, or perhaps of a different nature, and therefore, it can be stated that the actual influence of cold storage upon the chemical composition of flesh has not been accurately and properly determined.

It was therefore thought to be of interest, as has previously been stated, to make a preliminary chemical study along the lines just suggested and thus to get a working basis for a more extensive and elaborate investigation upon the chemistry of cold storage flesh products.

EXPERIMENTAL.

The method of refrigerating beef in this country is to rapidly chill the carcass as soon as slaughtered in order to remove the animal heat and thus to prepare it for the cooling chamber. It is then transferred to a well-ventilated room where the air is properly dried and kept in circulation. The temperature of the room is generally about 34° F., but in cases of long storage it may be almost freezing. The meat is not allowed to freeze. In the case of fowl, the most satisfactory method is to gradually freeze them solid as soon as killed, either drawn or undrawn, and then to keep them in cold storage at 10° F. Technically speaking, the former procedure of preparing flesh for storage gives the chilled or refrigerated meats, and the latter method the frozen meats.

In the present study, three experiments are reported: two upon beef and one upon fowl. Two of the experiments upon beef relate to the uncooked meat held in storage for different periods of time. In the first, the analyses of eight wholesale cuts are given and in the second, the analyses of four wholesale cuts. The third experiment, which is upon uncooked fowl, consists of the analyses of one lot of fresh unstored chicken, two lots of drawn frozen chicken, and two lots of undrawn frozen chicken.

Experiment No. 1.—In this experiment which was made in December, 1905, a registered Hereford steer, 18 months old, and fed for the market by the Station in connection with an extensive feeding experiment, was slaughtered by a private cold storage company. The above-described method of preparing the animal for cold storage was followed as closely as possible. The two halves of the

carcass, after being chilled, were placed in cooling rooms at 33–35° F. After two days the left half was removed from cold storage and cut up by an experienced cutter. All the wholesale cuts, the analysis of only four being reported here, were freed from excessive visible fat, tendon and all bone. The portions of the resulting lean beef were each thoroughly sampled by grinding them in a chopper. The right half of the carcass was held in storage for 22 days or practically three weeks longer than the left half. In this case, the wholesale cuts, the round, rib, plate, and full loin were freed from excessive visible fat, tendon, and all bone. The lean meats were then sampled in the same manner as those obtained from the left half and analyzed. From the several data, we have, on the one hand, to compare the composition of the lean of the round, rib, plate, and full loin cuts held in cold storage for two days with the corresponding wholesale cuts of the right half of the same animal held in cold storage for 22 days. In the former case, the laboratory numbers are 1924, 1927, 1929, and 1926 respectively, and in the latter case, they are 1954, 1957, 1959, and 1956 respectively.

Experiment No. 2.—A well fed, registered Durham steer about one year old was used in this experiment. He was slaughtered in January, 1906, and prepared for cold storage in the manner described in Experiment 1. The two halves of the carcass were kept in cold storage 6 days when they were both removed and the square chuck and full loin cuts were taken from each. Those from the right half were immediately returned to cold storage and held there for 37 days more or practically five weeks at a temperature of 33 to 35° F. The cuts from the left half were immediately sampled as in the previous experiment and analyzed. The cuts from the right half were also prepared for analysis in this manner. The laboratory numbers for these samples are for left chuck and loin 1993 and 1988, and for the right corresponding cuts 1973 and 1969, respectively.

The data obtained in these two experiments are assumed to be more comparable, when calculated to the same basis, than if the samples for examination had been taken from neighboring cuts of one-half or from corresponding cuts of different animals which had not necessarily been raised in the same locality. It can hardly be doubted that the lean of the corresponding cuts of the right and left half of the same animal are essentially the same chemically, while data herein reported show that the same wholesale cuts from the same half of different animals are not necessarily alike.

Experiment No. 3.—In this experiment, cold storage frozen drawn poultry are compared with undrawn fowl similarly prepared and kept, and further, fresh unstored poultry are compared with drawn and undrawn frozen fowl. The first lot, laboratory No. 2057, was undrawn, frozen, and held in storage for 21 months. The second lot, laboratory No. 2110, was drawn, frozen, and held in storage for an unknown period. The third lot, laboratory No. 2111, was undrawn, frozen and held in storage 4 months. The fourth lot, laboratory No. 2112, was drawn, frozen, and kept in storage 4 months. The fifth lot, laboratory No. 2067, was unstored and fresh. Lots three, four, and five were procured and prepared at the same time. In all cases the fowl when selected appeared perfectly sound. Nothing was known as to the strain, or kind of poultry, or as to their feed or the methods of preparing them for the market. The third, fourth and fifth lots of poultry were killed, dressed, and packed by a large wholesale firm in Chicago, under the direction and continuous supervision of one of us. The same day that the poultry were killed and dressed, they were placed in one of the best cold storage warehouses in Chicago and immediately frozen. The storage poultry was maintained at a temperature of 10° F. The fact should here be noted that this supply of poultry used in our investigation was immediately placed in cold storage after it was killed and dressed. The dressed poultry was not allowed to stand nor was it shipped from outlying districts before being stored.

In preparing the samples for analysis, several chickens were taken from each lot and thus a fair representative of the lots was obtained. The skin and any large lumps of fat were removed. After removal of the bone, the flesh thus obtained in each case was ground in the chopper, and then sampled and analyzed.

CHEMICAL METHODS USED.

In making the chemical study of the cold storage samples of flesh for these experiments, the methods used in the chemical analysis were essentially the ones as previously published from this laboratory.[1] Briefly stated the customary method of analyzing flesh was modified so as not only to aid in adding

[1] Grindley and Emmett, *Journ. Amer. Chem. Soc.*, **27**, 658–678 (1905). Emmett and Grindley, *Ibid.*, **28**, 25–63 (1906).

much more to our limited specific knowledge of the subject but to give a systematic and applicable means of ascertaining these data.

The ordinary method as used by all experiment stations, consisted mainly in determining, in the air-dried samples, the total nitrogen, total ash, fat, and moisture. The first improvement lay in the fact that it was found that fresh flesh could be so sampled that it could be analyzed directly without previously air-drying it. Naturally, this gave a ready and more rapid means of determining the above four constituents. Further, it did away with the questionable changes that take place in the air-drying of the sample such as the coagulation and cleavage of some of the proteins and the possible loss of nitrogen, volatile fatty acids, etc. The second step was the adoption of the method of extracting the fresh sample with cold, neutral, distilled water. By this means, a distinct differentiation was made in separating out several of the important constituents of flesh. Among the constituents so separated are: first, those substances which are most easily digested and of service in the nutritional economy as the albumins, some of the globulins, the proteoses, and any protamins; second, those substances which are thought to contribute in part to the flavor of cooked meats and to aid in stimulating the action of the gastric glands, as the nitrogenous extractives, of which creatin and the purin bases in some complex combination are members; third, those substances which aid in furnishing heat and energy to the body as the non-nitrogenous extractives, glycogen and para-lactic acid, the latter being also considered by some to play a part in the ripening of meats; and fourth, those substances which aid in maintaining the osmotic pressure of the body liquids, assist in carrying on the normal functions of irritability of muscle and nerve, and add flavor or increase the palatability of the cooked meats as sodium chloride, potassium chloride, potassium phosphates, and doubtless some calcium salts. The next improvement in the method was the estimation of the different forms of phosphorus and more especially the soluble phosphorus according to a modification of Hart and Andrews' method[1] of separating the inorganic and organic forms in seeds and seedlings. By this means the total soluble, the soluble inorganic, the soluble organic, the insoluble and the total phosphorus were estimated. The data thus obtained upon phosphorus were found to give an insight into the differences in the flesh from animals of different ages, in the different cuts of meat, in cooked meats, and in broths.

[1] *Am. Chem. J.*, **30**, 470 (1903).

In applying this method of analysis to the cold storage flesh, the following determinations are reported: (*a*) Water-soluble matter, including the coagulable, the non-coagulable, the protein, the non-protein, and total nitrogen; the coagulable, the non-coagulable, and total protein; the nitrogenous, non-nitrogenous, and total organic extractives; the ash; and the inorganic, organic, and total phosphorus. (*b*) Water-insoluble matter, including the total nitrogen; the protein; the fat; the ash; and the phosphorus. (*c*) Total matter, including the water; the dry substance; the protein; the nitrogen; the phosphorus; the ash; and the fat.

It should be added in connection with the chemical analysis, that at the time of making this preliminary study upon cold storage flesh, the methods of determining creatin,[1] ammonia,[2] and total acidity were not sufficiently developed for use.

DISCUSSION.

In the following discussion, first, the data for the refrigerated uncooked beef will be taken up, this including Experiment 1, where the halves of beef were held in cold storage for two days and three weeks, and also Experiment 2, where the chuck and loin wholesale cuts of the right and left halves were kept in storage for periods of 6 and 43 days; second, the drawn and undrawn frozen fowl will be studied; third, the drawn and undrawn frozen fowl will be compared with the fresh fowl; and fourth the differences in the cases of refrigerated uncooked beef and the frozen fowl will be contrasted.

THE INFLUENCE OF COLD STORAGE UPON UNCOOKED BEEF.

Fresh Substance.

In the two experiments which relate to uncooked beef, the data from the analysis of the lean of the twelve wholesale cuts are reported in Table I, as calculated in per cent. of the fresh substance.

It will subsequently be seen that these several data thus presented are not comparable from the standpoint in question. In the above paragraphs it was stated that in preparing the samples of beef for analysis, the excessive visible fat was first removed and the resulting lean meats were then taken for the chemical study.

[1] Grindley and Woods, *J. Biol. Chem.*, **2**, 309 (1907). Emmett and Grindley, *Ibid.*, **3**, 491 (1907).

[2] Gill and Grindley, *Science*, **27**, 497 (1908).

In the removal of the excessive fat in the trimming of the cuts, it was naturally quite impossible to make a quantitative separation from the lean and no attempt was made to do so. A glance at the data in Table I, Experiment 1, will show that in a number of instances the amount of fat remaining in the samples analyzed was more in some of the 2-day samples, while in others, it was less than in the 22-day samples. For example, in the plate cuts (1929 and 1959) the percentages of fat are 19.56 and 21.53 respectively, and in the loin cuts (1926 and 1956) they are 12.66 and 11.99 respectively. Such differences in the data, calculated to the fresh substance, influence in a reverse manner the percentages of the other constituents as is shown in this case where the data in Table I, Experiment 1, indicate that the round cut (1954), the rib cut (1957), and the plate cut (1959) lost, during the storage of 20 days, from 1 to 1.7 per cent. of water, while the loin cut (1956) showed no change. Similarly, the data of Experiment 2, show that the chuck cut (1993) gained during the cold storage period of 37 days 1 per cent. of water and the loin cut (1988) lost 0.6 per cent., all of which is quite contradictory to the general expectation and belief.

Further, attention should be called to the fact that if the data from the analysis of the lean beef were calculated to the original fat content of the wholesale cut, the resulting figures would show similar variations to those above for the corresponding cuts. In Table I, the total percentages of fat and water calculated to the wholesale cut without bone are given in brackets to illustrate this fact. In the rib cuts (1927 and 1957), the percentages of fat are 36.02 and 35.55 respectively which are nearly the same, while in the loin cut (1926) it is 34.76 per cent. and in the corresponding cut (1956), it is 30.79—a difference of 4 per cent.

It is evident from the above statements, that the

TABLE I.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH.

EXPERIMENT 1.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Fresh Substance.)

Description of sample	Lean beef, round.		Lean beef, rib.		Lean beef, plate.		Lean beef, loin.	
Laboratory No.	1924	1954	1927	1957	1929	1959	1926	1956
Time held in cold storage (days)	2	22	2	22	2	22	2	22
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water:								
In fresh substance	71.29	70.19	65.92	64.45	61.66	59.98	67.26	67.27
In original wholesale cut	(61.75)	(61.98)	(49.08)	(49.28)	(40.69)	(42.72)	(50.02)	(52.84)
Dry substance:								
Soluble	5.77	5.72	4.77	4.85	4.25	3.81	5.57	5.33
Insoluble	22.67	24.11	29.70	31.17	34.22	36.06	27.96	27.61
Total	*28.44*	*29.83*	*34.47*	*36.02*	*38.47*	*39.87*	*33.53*	*32.94*
Protein:								
Soluble coagulable	2.29	2.04	1.77	1.88	1.45	1.37	2.06	1.90
Soluble non-coagulable	0.15	0.25	0.18	0.26	0.17	0.20	0.21	0.20
Total	*2.44*	*2.29*	*1.95*	*2.14*	*1.62*	*1.57*	*2.27*	*2.12*
Insoluble	16.18	15.85	15.10	15.12	14.55	14.33	15.26	15.52
Total	*18.62*	*18.14*	*17.05*	*17.26*	*16.17*	*15.90*	*17.53*	*17.64*
Organic extractives:								
Nitrogenous	1.24	1.14	0.99	0.89	0.88	0.74	1.15	1.07
Non-nitrogenous	1.22	1.37	1.06	1.09	1.01	0.95	1.35	1.29
Total	*2.46*	*2.51*	*2.05*	*1.98*	*1.89*	*1.69*	*2.50*	*2.36*
Fat (by ether):								
In fresh substance	6.32	8.20	14.46	15.90	19.56	21.53	12.66	11.99
In original wholesale cut	(18.73)	(17.84)	(36.02)	(35.55)	(46 56)	(43.99)	(34.76)	(30.79)
Ash:								
Soluble	0.87	0.92	0.77	0.73	0.74	0.55	0.80	0.85
Insoluble	0.17	0.06	0.14	0.15	0.11	0.20	0.04	0.10
Total	*1.04*	*0.98*	*0.91*	*0.88*	*0.85*	*0.75*	*0.84*	*0.95*
Nitrogen:								
As soluble coagulable protein	0.366	0.326	0.284	0.300	0.233	0.219	0.329	0.304
As soluble non-coagulable protein	0.024	0.040	0.028	0.043	0.026	0.031	0.034	0.035
Total	*0.390*	*0.366*	*0.312*	*0.343*	*0.259*	*0.250*	*0.363*	*0.339*
As soluble non-protein substance	0.396	0.366	0.317	0.286	0.282	0.237	0.368	0.342
Total	*0.786*	*0.732*	*0.629*	*0.629*	*0.541*	*0.487*	*0.731*	*0.681*
Insoluble	2.588	2.537	2.416	2.418	2.328	2.294	2.442	2.483
Total	*3.374*	*3.269*	*3.045*	*3.047*	*2.869*	*2.781*	*3.173*	*3.164*
Phosphorus:								
Soluble inorganic	0.098	0.118	0.097	0.105	0.078	0.096	0.096	0.110
Soluble organic	0.050	0.052	0.042	0.043	0.052	0.029	0.045	0.044
Total	*0.148*	*0.170*	*0.139*	*0.148*	*0.130*	*0.125*	*0.141*	*0.154*
Insoluble	0.082	0.055	0.055	0.046	0.053	0.044	0.072	0.061
Total	*0.230*	*0.225*	*0.194*	*0.194*	*0.183*	*0.169*	*0.213*	*0.215*

TABLE I.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH—(*Continued*).

EXPERIMENT 2.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Fresh Substance.)

Description of sample	Lean beef, chuck.		Lean beef, loin.	
Laboratory No.	1973	1993	1969	1988
Time held in cold storage (days)	6	43	6	43
	P. ct	P. ct.	P. ct.	P. ct.
Water:				
In fresh substance	70.71	71 69	71.12	70.50
In original wholesale cut	(60.77)	(61.03)	(56.27)	(54.18)
Dry substance:				
Soluble	4.81	5.56	5.52	6.43
Insoluble	24.37	23.26	23.18	23.88
Total	*29.22*	*28.82*	*28.70*	*30.31*
Protein:				
Soluble coagulable	1.68	2.05	2.03	2.13
Soluble non-coagulable	0.26	0.22	0.18	0.28
Total	*1 94*	*2.27*	*2.21*	*2.41*
Insoluble	15.66	16.34	15.69	15.93
Total	*17.60*	*18.61*	*17.90*	*18.34*
Organic extractives:				
Nitrogenous	0 89	1.02	1 02	1.26
Non-nitrogenous	1.24	1.55	1 44	1.89
Total	*2.13*	*2.57*	*2 46*	*3.15*
Fat (by ether).				
In fresh substance	8.51	6.69	7.35	7.76
In original wholesale cut	(20.98)	(19.67)	(26.02)	(28.77)
Ash:				
Soluble	0.78	0.72	0.85	0.87
Insoluble	0.20	0 23	0 14	0.17
Total	*0.98*	*0 95*	*0.99*	*1.04*
Nitrogen:				
As soluble coagulable protein	0.268	0.328	0 325	0 340
As soluble non-coagulable protein	0.042	0.035	0.029	0.045
Total	*0.310*	*0 363*	*0.354*	*0.385*
As soluble non-protein substance	0.285	0.325	0.329	0.405
Total	*0.595*	*0.688*	*0.683*	*0.790*
Insoluble	2.506	2.614	2.510	2.549
Total	*3 101*	*3 302*	*3.195*	*3.339*
Phosphorus:				
Soluble inorganic	0.097	0 125	0 101	0 134
Soluble organic	0.047	0.018	0.056	0.064
Total	*0.144*	*0.143*	*0.157*	*0.198*
Insoluble	0.069	0.085	0.083	0.017
Total	*0 213*	*0.228*	*0.240*	*0 215*

data of the lean of the beef of the wholesale cuts, when calculated as in Table I, upon the fresh basis, cannot be compared directly as to the chemical changes which may have taken place during cold storage, and it is also evident that if this data were calculated back to the original fat content, they would still not be strictly comparable for the same reasons. Therefore, in order to remove both the small and large errors and put the data upon a fair basis for comparison, all the results for the experiments were calculated to the fat-free basis as shown in Table II.

Fresh Substance, Calculated to the Fat-free Basis.

Chemical composition of cold storage uncooked beef, calculated to the fat-free basis: In considering the results of Experiments 1 and 2, where the difference in time of storage of the several corresponding cuts was 20 days in the former case and 37 days in the latter, it will be seen, as regards the general opinion that meats lose water during cold storage, that of the 22-day samples only one shows any apparent decrease. It should be noted in this connection that the air of the storage room in which these meats were kept was moist, thus preventing to a considerable extent desiccation. The percentages of water in the round, plate, and loin cuts are practically the same, while in the rib cut (1957), it is 0.51 per cent. lower than in the corresponding cut (1927). The averages of these four respective samples are 76.47 per cent. for the 2-day period and 76.38 per cent. for the 22-day period, showing a difference of only 0.09 per cent. On the other hand, the chuck and loin cuts in Experiment 2 show that during the 37-day period there was a distinct loss of water, there being a decrease of 0.94 per cent. for the former (1993) and 1.13 per cent. for the latter (1988), with an average difference of 1.04 per cent. This distinct loss of moisture

in Experiment 2 may be explained in three ways: first, as due to the additional time during which the meats were held in cold storage; second, to the fact that these wholesale cuts (1993 and 1988) were cut from the right half at the same time that the corresponding ones (1973 and 1961) were cut from the left half, and hence the difference in the size of the pieces might possibly allow of a more extensive drying out during the subsequent period of cold storage than in the case of Experiment 1 where the entire halves were allowed to hang; and third, to the fact that the air of the storage room was not as moist as it was in the case of Experiment 1. Müller,[1] however, claims that the size of the cut bears no relation to the percentage of loss of water during the period of hanging in cold storage.

In Experiment 1, the soluble dry substance tends to increase slightly during storage in the round cut (1954) and in the rib cut (1957), the maximum amount being in the latter 0.18 per cent., which is 3.2 per cent. of the total soluble dry substance. The plate (1959) and loin (1956) cuts show a decrease of from 0.41 to 0.28 per cent. respectively, or 7.7 to 4.4 per cent. of their total amounts. The averages in all four cases are 5.83 per cent. for the 2-day samples and 5.71 per cent. for the 22-day samples which indicates very little difference due to storage. The data in Experiment 2 are noticeably higher in soluble dry substance in the samples held in storage for a longer time. In the chuck cut (1973) the percentage of water-soluble dry substance is 5.30, while in the corresponding cut (1993) which was stored 37 days longer, it is 5.92, or 11.7 per cent. gain. In the loin cuts (1969 and 1988) the respective percentages of soluble dry substance are 5.97 and 6.91, showing a gain of 15.75 per cent. The average of the two cuts indicates a difference in the constituents of 0.78 per cent. which is equal

TABLE II.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH.

EXPERIMENT 1.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Fat-free Basis.)

Description of sample	Lean beef, round		Lean beef, rib.		Lean beef, plate.		Lean beef, loin.		Average of (4).	Average of (4).
Laboratory No.	1924	1954	1927	1957	1929	1959	1926	1956		
Time held in cold storage (days)	2	22	2	22	2	22	2	22	2	22
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	76.32	76.44	76.71	76.20	76.53	76.58	76.32	76.25	76.47	76.38
Dry Substance:										
Soluble	6.18	6.23	5.55	5.73	5.27	4.86	6.32	6.04	5.83	5.71
Insoluble	17.50	17.32	17.74	18.07	18.20	18.56	17.36	17.71	17.70	17.92
Total	*23.68*	*23.55*	*23.29*	*23.80*	*23.47*	*23.42*	*23.68*	*23.75*	*23.53*	*23.63*
Protein:										
Soluble coagulable	2.45	2.23	2.06	2.21	1.80	1.75	2.34	2.15	2.16	2.09
Soluble non-coagulable	0.16	0.27	0.21	0.32	0.21	0.25	0.24	0.25	0.21	0.27
Total	*2.61*	*2.50*	*2.27*	*2.53*	*2.01*	*2.00*	*2.58*	*2.40*	*2.37*	*2.36*
Insoluble	17.32	17.26	17.57	17.90	18.06	18.31	17.32	17.60	17.57	17.79
Total	*19.93*	*19.76*	*19.84*	*20.43*	*20.07*	*20.31*	*19.90*	*20.00*	*19.94*	*20.13*
Organic extractives:										
Nitrogenous	1.32	1.24	1.15	1.05	1.09	0.95	1.30	1.21	1.21	1.11
Non-nitrogenous	1.31	1.49	1.23	1.29	1.25	1.21	1.53	1.46	1.33	1.36
Total	*2.63*	*2.73*	*2.38*	*2.34*	*2.34*	*2.16*	*2.83*	*2.67*	*2.54*	*2.47*
Ash:										
Soluble	0.93	1.00	0.90	0.86	0.92	0.70	0.91	0.97	0.91	0.88
Insoluble	0.18	0.06	0.16	0.18	0.14	0.26	0.04	0.11	0.13	0.15
Total	*1.11*	*1.06*	*1.06*	*1.04*	*1.06*	*0.96*	*0.95*	*1.08*	*1.04*	*1.03*
Nitrogen:										
As soluble coagulable protein	0.392	0.355	0.330	0.355	0.289	0.280	0.373	0.344	0.346	0.334
As soluble non-coagulable protein	0.026	0.044	0.033	0.051	0.032	0.040	0.039	0.040	0.032	0.043
Total	*0.418*	*0.399*	*0.363*	*0.406*	*0.321*	*0.320*	*0.412*	*0.384*	*0.378*	*0.377*
As soluble non-protein substance	0.423	0.399	0.369	0.338	0.350	0.302	0.417	0.388	0.390	0.357
Total	*0.841*	*0.798*	*0.732*	*0.744*	*0.671*	*0.622*	*0.829*	*0.772*	*0.768*	*0.734*
Insoluble	2.771	2.762	2.812	2.861	2.889	2.929	2.771	2.814	2.811	2.841
Total	*3.612*	*3.560*	*3.544*	*3.605*	*3.560*	*3.551*	*3.600*	*3.586*	*3.579*	*3.575*
Ratio of non-protein to protein:										
In water extract	1:0.98	1:1.00	1:0.98	1:1.20	1:0.92	1:1.06	1:0.99	1:0.99	1:0.97	1:1.06
In meats	1:7.52	1:7.92	1:8.60	1:9.67	1:9.17	1:10.74	1:7.63	1:8.24	1:8.18	1:9.01
Phosphorus:										
Soluble inorganic	0.104	0.128	0.113	0.124	0.097	0.123	0.109	0.125	0.106	0.125
Soluble organic	0.053	0.056	0.049	0.051	0.064	0.037	0.051	0.050	0.054	0.048
Total	*0.157*	*0.184*	*0.162*	*0.175*	*0.161*	*0.160*	*0.160*	*0.175*	*0.160*	*0.173*
Insoluble	0.088	0.060	0.064	0.054	0.066	0.056	0.082	0.069	0.075	0.060
Total	*0.245*	*0.244*	*0.226*	*0.229*	*0.227*	*0.216*	*0.242*	*0.244*	*0.235*	*0.233*

[1] *Loc. cit.*

TABLE II.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH.—(*Continued*).

EXPERIMENT 2.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Fat-free Basis.)

Description of sample	Lean beef, chuck.		Lean beef, loin.		Average of (2).	Average of (2).
Laboratory No.	1973	1993	1969	1988		
Time held in cold storage (days)	6	43	6	43	6	43
	P. ct	P. ct.	P. ct.	P. ct	P. ct.	P. ct.
Water	77.35	76.41	76.91	75.78	77.13	76.09
Dry Substance:						
Soluble	5.30	5.92	5.97	6.91	5.63	6.41
Insoluble	17.35	17.67	17.12	17.31	17.23	17.49
Total	*22.65*	*23.59*	*23.09*	*24.22*	*22.87*	*23.90*
Protein:						
Soluble coagulable	1.84	2.18	2.20	2.29	2.02	2.24
Soluble non-coagulable	0.28	0.23	0.19	0.30	0.23	0.26
Total	*2.12*	*2.41*	*2.39*	*2.59*	*2.25*	*2.50*
Insoluble	17.13	17.43	16.97	17.12	17.05	17.27
Total	*19.25*	*19.84*	*19.36*	*19.71*	*19.30*	*19.77*
Organic extractives:						
Nitrogenous	0.98	1.09	1.10	1.35	1.04	1.22
Non-nitrogenous	1.35	1.65	1.56	2.03	1.45	1.84
Total	*2.33*	*2.74*	*2.66*	*3.38*	*2.49*	*3.06*
Ash:						
Soluble	0.85	0.77	0.92	0.94	0.89	0.85
Insoluble	0.22	0.24	0.15	0.19	0.18	0.22
Total	*1.07*	*1.01*	*1.07*	*1.13*	*1.07*	*1.07*
Nitrogen:						
As soluble coagulable protein	0.293	0.350	0.351	0.366	0.322	0.358
As soluble non-coagulable protein	0.046	0.037	0.032	0.048	0.039	0.042
Total	*0.339*	*0.387*	*0.383*	*0.414*	*0.361*	*0.400*
As soluble non-protein substance	0.312	0.346	0.356	0.435	0.334	0.391
Total	*0.651*	*0.733*	*0.739*	*0.849*	*0.695*	*0.791*
Insoluble	2.741	2.786	2.714	2.740	2.727	2.727
Total	*3.392*	*3.519*	*3.453*	*3.589*	*3.422*	*3.554*
Ratio of non protein to protein:						
In water extract	1: 1.09	1: 1.12	1: 1.07	1: 1.95	1: 1.08	1: 1.02
In meats	1: 9.87	1: 9.17	1: 8.44	1: 7.24	1: 9.11	1: 8.09
Phosphorus:						
Soluble inorganic	0.106	0.133	0.109	0.144	0.107	0.139
Soluble organic	0.051	0.019	0.061	0.069	0.056	0.044
Total	*0.157*	*0.152*	*0.170*	*0.213*	*0.163*	*0.183*
Insoluble	0.076	0.091	0.090	0.018	0.083	0.054
Total	*0.233*	*0.243*	*0.260*	*0.231*	*0.246*	*0.237*

to 13.9 per cent. of the total amount. This gain is sufficient to show that in Experiment 2 there is a distinct difference from Experiment 1 in the water-soluble dry substance.

The percentages of insoluble dry substance in the samples of beef of the first experiment are inclined to be a little high in the meats which were refrigerated for 22 days. This difference is due chiefly to a corresponding increase in the insoluble protein. The one exception to this statement is in the round cut (1954) which is 0.18 per cent. lower in insoluble dry substance and 0.06 per cent. in insoluble protein. The other cuts, the rib (1957), the plate (1959) and the loin (1956) are each about 0.35 per cent. higher, showing an average for the four 2-day samples of 17.70 per cent. and for the 22-day samples of 17.92 per cent., which is equivalent to a gain of only 1.2 per cent. The chuck and loin cuts in Experiment 2 are a little higher in insoluble dry substance for the samples held in storage for 43 days, being in the former case 0.32 per cent. and in the latter 0.19 per cent. with an average increase of 0.26 per cent., or a percentage gain of 1.5. Compared in this respect, there is very little difference in the insoluble dry substance between the meats held in storage for the 2- and 22-day periods and those for 6- and 43-day periods. Concerning the total dry substance, it can be stated that, with the exception of the rib cut (1957), the data for the 22-day samples are almost identical to those for the 2-day samples. The rib cut shows a gain of 0.51 per cent., due in the main to the loss of water. The average of the respective four cuts are 23.53 and 23.63 per cent. The data for the second experiment, however, show an increase of 0.94 per cent. for the chuck cut (1993) and of 1.13 per cent. for the loin cut (1988), making an average gain of 1.03 per cent. in total dry substance which is 4.5 per cent. of the total.

A comparison of the above various forms of dry substance indicates from the data in the two

experiments that the meats held in storage for 43 days made a distinct gain over those held for 22 days in the soluble form, a slight one in the insoluble form and a distinct one in the total.

Regarding the different forms of protein in these experiments, practically nothing can be stated of the coagulable form. The differences in this form in the first experiment are slight and variable, averaging 2.16 and 2.09 per cent. of the coagulable protein present for the 2- and 22-day samples, while in the second experiment, the 37-day samples show a tendency to gain, being for the chuck cut (1993), an increase of 0.34 per cent. and for the loin cut (1988), an increase of only 0.09 per cent. The non-coagulable protein which includes any peptones that may be present, in the first test increases throughout the four samples, but in two of the cases, the loin and the plate cuts, the gains, 0.01 and 0.04 per cent., are so small that they may be considered within the limits of the errors of the method. The other two cases (1954 and 1957), the round and rib cuts respectively, are decidedly higher, being in the former 0.27 per cent. against 0.16 per cent. and in the latter 0.32 per cent. against 0.21 per cent. However, the total gain in these two cases is not of an amount to be of any value in indicating decomposition of the flesh by supposing the gain to be due solely to peptones; especially is this true if we take into consideration the averages of the 2- and 22-day samples which are 0.21 and 0.27 per cent. respectively. These same statements apply to Experiment 2 where the comparative period of cold storage is 37 days. In the chuck cut (1993) there is a decrease, 0.05 per cent. of the non-coagulable protein and in the loin cut (1988) an increase of 0.11 per cent. on 0.19 per cent. The fact that these differences in the 37-day period are no greater than in the 20-day period tends to further confirm the statement that the increase in the non-coagulable protein is not due to bacterial decomposition.

The influence of cold storage upon the total soluble protein is very slight in Experiment 1. Here, the differences are variable, being noticeably high in but one case. This is in the 22-day rib cut (1957), where there is an increase of 0.26 per cent. The averages of total soluble protein for the corresponding 2- and 22-day cuts are 2.37 and 2.36 per cent. respectively. The data for experiment 2 show a slight gain in the total soluble protein for both of the cuts, being 0.29 and 0.20 per cent. respectively for the 37-day samples of the chuck and loin cuts, making an average increase of 0.24 per cent., which is 10.6 per cent. of the total soluble protein.

As stated, in considering the insoluble dry substance, the differences there were due, in the main, to similar differences in the insoluble protein. The increase in the insoluble protein is greater in the 37-day samples than in the 22-day samples, being on the average 0.22 per cent. in the first instance and 0.22 per cent. in the last one, which means a percentage gain of 1.3 and 1.2 respectively. The total protein in the two experiments is variable, in the first one, where the most distinct differences are in samples 1957 and 1959 which show the former to have 0.59 and the latter 0.24 per cent. more of the constituents than the corresponding 2-day samples. The other differences are no greater than those that might occur in duplicate analyses. The averages show a very slight gain: the 2-day stored meats have 19.94 per cent. of total protein and the 22-day meats 20.13 per cent. The samples of the second experiment have an increase in the total percentage of protein of 0.59 for the 43-day refrigerated chuck sample (1993) and one of 0.35 for the similar loin sample (1988). The averages of the two cuts are 19.30 per cent. for the 6-day refrigerated meats and 19.77 for those refrigerated 43 days, making a difference of 0.47 per cent. as against 0.19 per cent. in the 22-day samples, or a percentage gain of 2.4 in the former and 0.96 in the latter.

From this discussion upon the differences in the amounts of protein in the meats held in storage for periods of 22 and 43 days, the data indicate that the coagulable protein tends to be a trifle higher in the latter case, the non-coagulable to be about the same in both instances, the total soluble to be slightly higher in the second experiment and the insoluble and total protein to be somewhat higher in the 43-day tests. These differences in the data appear to be due mainly to the greater loss of water, but this point will be considered later.

Of the organic extractives in Experiment 1, the nitrogenous form, which is thought by some to contribute, at least in part, to the flavor of meat, shows, contrary to expectations, if this assumption be correct, a decrease throughout for the 22-day samples of about 0.10 per cent., or 8.2 per cent. of the total nitrogenous organic extractives present. On the other hand, in the refrigerated test for 43-day samples of meat, there is an increase in both cases, being in the chuck cut (1993) 0.11 per cent.

and in the loin cut (1988) 0.25 per cent., averaging 0.18 per cent. or 17.3 per cent. of the total amount. It is also significant to note in Experiment 1, the apparent constancy of the non-nitrogenous organic extractives, which, upon the theory that the ripening of meat is due to an increase in the sarcolactic acid, it would be expected to show an increase. In the second experiment, for the 37-day interval, these data for the non-nitrogenous extractives indicate a consistent gain for the 43-day samples, being 0.30 per cent. in the chuck cut, and 0.49 per cent. in the loin cut, averaging 0.39 per cent. against 0.03 per cent. in the 22-day samples of Experiment 1, or a percentage gain of 26.9 per cent. in the former case. The per cent. of total extractives is about the same in the corresponding 2- and 22-day samples. The slight differences are variable, being in some cases greater and in others less. The averages of the four cuts are for the former period 2.54 per cent., and for the latter period 2.47 per cent. For the second test, the percentage of total extractives is higher in the 43-day chuck and loin samples (1993 and 1988), being for the chuck 0.41 per cent. and for the loin 0.72 per cent., with an average increase for the two cuts of 0.57 per cent., which actually means a percentage increase of 22.9. This comparison of the data for the extractives tends to show that the samples of meat held in cold storage for 22 days did not approach the degree of ripeness, which would be indicated chemically by an increase in the different organic extractives, that the 43-day samples did, and hence the latter meats should be theoretically the more highly flavored and pleasing when cooked.

A study of the data relating to the forms of ash in both experiments shows nothing definite. The differences in nearly all cases are very slight. They are variable and not at all consistent and hence will not be considered in detail.

As regards the different kinds of nitrogen, those for the coagulable, the non-coagulable, and the total soluble protein, and the insoluble have been considered indirectly under the corresponding headings of the protein, since these latter were obtained by multiplying each of the former by 6.25. The non-protein nitrogen in Experiments 1 and 2 shows more distinctly the decrease in the 22-day samples and the increase in the 43-day samples than does the non-protein form proper, being about 8.5 per cent. for the former and 17.1 for the latter. In the case of the total soluble nitrogen, it will be seen that in Experiment 1, the 22-day samples are all, with the exception of the rib cut sample (1957), distinctly lower. Here the slight gain is due in part to the difference in water content and in part to the gain of protein nitrogen. The average for all the tests shows a difference in the soluble matter of 0.034 per cent. which is a decrease of 4.3 per cent. of the total. This lower percentage of nitrogen is accounted for in part by the decrease in the non-protein nitrogen and in part by the possible formation of acid albumen as a result of the effect of the increase of the soluble inorganic phosphate, and this explains further the increase in the coagulable nitrogen and insoluble nitrogen. In Experiment 2, the consistent gains of total soluble nitrogen in the 43-day samples are explained as due to similar gains in both the soluble protein and non-protein nitrogen. The averages for the 6- and 43-day samples are 0.695 per cent. for the former and 0.791 per cent. for the latter, making a difference of 0.096 per cent. which is equal to a gain of 13.8 per cent. The total nitrogen in Experiment 1, is quite variable in the first two samples, the round cuts (1924 and 1954) and the rib cuts (1927 and 1957). In the first case, there is a loss for the 22-day sample of 0.052 per cent. out of a total of 3.612 per cent., while in the second case there is a gain of 0.061 per cent. on a total of 3.544 per cent. The other two samples, the plate and loin cuts, are slightly lower than those held in storage for a longer period. The average per cent. of the total nitrogen for the two sets is for the 2-day samples 3.579 and for the 22-day samples 3.575, which is very close. Likewise, in considering this form of nitrogen, the total in the second experiment, there is a noticeable gain in both the chuck and loin cuts, which were kept in cold storage for 43 days, against those kept for 6 days, being for the first samples 3.392 and 3.519 per cent., and for the second samples 3.453 and 3.589 per cent., making an average per cent. of 3.422 for the 6-day and 3.554 for the 43-day period, which is 0.132 per cent. or a percentage gain of 3.8.

Further, it will be of interest in the consideration of the forms of nitrogen to note the influence of the above-mentioned variances upon the ratio of the non-protein to the total soluble protein, and to the total protein nitrogen. In but one instance, in the two experiments, is there any marked difference in the ratios of the non-protein nitrogen to the soluble protein. This variation is in the case of the 2- and 22-day samples of the rib cut, experi-

ment 1 (1927 and 1957), but it is not sufficient to modify the statement that these ratios remain nearly constant throughout the two tests showing that the changes which took place in the non-protein nitrogen were either slight or that they occurred in almost a similar proportion to those in the soluble protein nitrogen. Regarding the ratios of the soluble non-protein nitrogen to the total protein nitrogen, that is, the soluble and insoluble forms combined, the data in Experiment 1 show an appreciable increase in each of the 22-day samples, averaging for all 1:9.01 against 1:8.18 in the 2-day samples. This is due to the fact that the non-protein nitrogen in the 22-day sample is 8.5 per cent. lower and the insoluble protein nitrogen a trifle higher, 1.1 per cent., throughout this series. In the case of Experiment 2, the reverse condition seems to be true. The ratios of the non-protein to the total protein nitrogen are lower in both of the 43-day samples as compared with the 6-day samples. The averaged calculated ratios are 1:8.09 in the former case and 1:9.11 in the latter. This is explained in part, that like the above instance the insoluble protein nitrogen is higher, 1.7 per cent., in the samples which were held in cold storage for the longer period, but unlike it, these samples were also higher in the non-protein and soluble protein nitrogen, having a gain of 17.0 and 10.8 per cent. respectively. However, while this increase of the protein nitrogen is considerably greater than that in Experiment 1, the gain in the non-protein nitrogen is still greater and as a result the ratios in the 43-day samples are lower than in the 6-day samples.

Of the various forms of phosphorus, the water-soluble inorganic shows, perhaps, the most consistent and appreciable differences. In Experiment 1 the data for the inorganic phosphorus show a distinct increase in the 22-day samples, being a gain in every case of from 0.011 per cent. in the rib cut to 0.026 per cent. in the plate cut. The averages for all four cuts are in the 2-day samples 0.106 per cent. of phosphorus and on the 22-day samples 0.125 per cent., making a percentage gain of about 17.9. In Experiment 2 the inorganic phosphorus shows the same tendency to be higher in the samples held in cold storage for the longer period, 43 days. Here, the average for the two cuts are 0.107 per cent. for the 6-day samples and 0.139 per cent. for the others. This means an increase of phosphorus in the latter case of 29.9 per cent. The soluble organic and total soluble phosphorus in the corresponding samples of Experiments 1 and 2 show no consistent variations throughout. The general tendency of the total soluble forms in the meats held in cold storage for the longer time is to be either practically the same or a little higher than that in the samples kept for the short periods. In both experiments, the percentage averages are higher in the 22- and 43-day meats, being in Experiment 1, 0.160 and 0.173 and in Experiment 2, 0.163 and 0.183 respectively for the short and long periods. The insoluble phosphorus in Experiment 1 shows a tendency to be lower in every case in the 22-day samples, being on the average 0.015 per cent., or calculated in per cent. of the total a decrease of 20.0 per cent. In Experiment 2 this form of phosphorus is higher in the 43-day samples for the chuck (1993), but on the other hand it is decidedly lower for the loin cut (1988), so much so that the result must be considered as questionable. Regarding the total phosphorus, it will be seen in the first experiment that there is practically no difference in the amounts in the 2- and 22-day samples. The average in the former case is 0.235 per cent. and in the latter 0.233 per cent. In the second experiment, however, little can be said since, as just cited, the determination in the 43-day loin sample (1988) of the insoluble phosphorus which is gotten by subtracting the total soluble from the total phosphorus, seems to be unreliable, apparently due to the low per cent. of total phosphorus.

From the foregoing consideration of the different forms of phosphorus, the data show: First, pretty conclusively that the percentage of the water-soluble inorganic phosphorus is higher in the meats which have been kept in cold storage for the longer periods and that the averages in these cases seem to indicate on the whole that the longer the time of storage, the greater is the tendency of the inorganic phosphorus to increase. This gain in inorganic phosphorus does not show any apparent definite source. In some cases, it seems to be derived from the organic forms, in others, from the insoluble form, and again in others from both of them. It is significant to note in this connection, since the data in Experiment 1 show so slight an increase in the non-nitrogenous organic extractives which includes lactic acid, that the first stage in the acidity and the ripening of meat is due rather to the increase of the inorganic phosphates. This fact tends to confirm the conjectures of several physiologists. Second, the data show that the

percentage of total soluble phosphorus of the meats kept in cold storage for the longer periods is slightly higher. Third, the data indicate that in Experiment 1 the amount of insoluble phosphorus is lower in the 22-day samples, and, fourth, that the percentage of total phosphorus in these same meats is practically identical with those in the 2-day samples.

From the above detailed discussion of the data in Experiments 1 and 2, calculated to the fat-free basis, the following general summary can be made: First, as regards the eight samples in Experiment 1, which were kept in cold storage at about 33° F. for 2 and 22 days respectively, the average results of the chemical study show that very few changes took place in the latter samples during the 20-day interim. There was practically no loss of water and total nitrogen and no appreciable gain in water-soluble dry substance, soluble protein, non-nitrogenous organic extractives, and total phosphorus. There was an apparent slight tendency of an increase in the insoluble dry substance, the coagulable protein, the insoluble protein, the total protein, and the total soluble phosphorus. And, finally, the only consistent changes of real note were the decrease of 8.5 per cent. in the non-protein nitrogen and accordingly in the nitrogenous organic extractives, and also a slight decrease in the total soluble nitrogen and an increase of 17.9 per cent. in the soluble inorganic phosphorus. These statements show conclusively that as far as these data are concerned, the meats which were held in cold storage for practically three weeks were just as nutritious as were those which had been kept for only two days. Further, they indicate that the intra-chemical changes were exceedingly few and that there was nothing as far as the increase in proteose and peptones were concerned, to prove any kind of decomposition to have occurred during this time.

Second, as regards the four samples in Experiment 2, the data here reported show that when the meats were kept in cold storage for 43 days or three weeks longer than those in Experiment 1, the proportional distribution of the several constituents in the samples which were held for the entire period, in the former case underwent more changes than those which were held in storage for 22 days, as in the first experiment. Here, the results show that an appreciable loss of moisture took place during the six weeks, being on an average 1.04 per cent. or 1.3 per cent. of the total. Naturally, this decrease in the water content effected the percentages of total dry substance in a reverse manner, increasing it 1.04 per cent. or making a total percentage gain, on this assumption, of 4.6 per cent. This total gain is distributed between the soluble and insoluble forms of dry substance, being in the former case 3.4 and in the latter 1.1 per cent. of the total or in per cent. of their respective total amounts 13.8 and 1.5 per cent. However, these proportional gains in the soluble and insoluble dry substances, and therefore in many of the constituents, are not necessarily alone due to the loss of water but are, as will be seen in a subsequent discussion, in part effected by other influences during the cold storage period.

The data for the other chemical constituents reported show consistent gains in both the chuck and loin cuts, being for the soluble, insoluble, and total protein 11.1, 12.9, and 2.4 per cent. respectively of the total amounts in each case; for the nitrogenous, non-nitrogenous, and total organic extractives, respectively 17.3, 26.9, and 22.9 per cent. of the amount in the 6-day samples; for the coagulable nitrogen 10.2 per cent., the total soluble, the insoluble, and total protein nitrogen 10.8, 1.3, and 2.4 per cent. respectively; the non-protein nitrogen 16.6 per cent. and the total soluble, insoluble, and total nitrogen 13.8, 1.3, and 3.9 per cent.; and finally for the inorganic and total soluble phosphorus 29.9 and 12.3 per cent. respectively.

From these statements regarding the data herein reported of Experiment 2, Table II, calculated to the fat-free basis, it must be concluded when comparing the meats which were kept in cold storage for 43 days with similar ones kept in storage for 6 days, that during the 37-day interval the former became somewhat drier, higher in the soluble, and total protein nutrients, also higher in the different organic extractives and in soluble phosphates, while the non-coagulable protein which includes any peptones, showed no greater change than in the former experiment. These facts all indicate, chemically, that these meats, during the cold storage period, had retained their full nutritive value.

Fat-Free Substance Calculated to the Same Water Content.

Chemical Composition of Cold Storage Uncooked Beef, Calculated to the Same Water Content.—In considering further the data in Table II, calculated to the fat-free basis, it will be recalled that

the differences in the chemical composition of the meats, which were kept in storage for varying lengths of time, were much greater in the second experiment than in the first one, and since there was a noticeable loss of water in the former case, and almost none in the latter, it might be assumed that these variances were due primarily and solely to the drying out of the meat, a fact which is claimed by some investigators. In order to ascertain an idea of the exact state of affairs in this connection, the data in Table II were calculated so as to represent as nearly as possible the chemical changes, other than the loss of moisture, which took place during the storage. By so doing, the data should represent, in comparing it with that just discussed, whether the changes in the percentage of the constituents during cold storage were due to loss of water only, and consequently something regarding the actual intra-chemical rearrangement due to the so-called ripening of meats. With these objects in view, the data as presented in Table II were so calculated that the analysis of the corresponding cuts, which were kept in cold storage for the entire period, are upon the same moisture basis as those kept for the shorter time. Table III shows the results in this form.

It will be seen from the data that the only noticeable differences produced by the recalculation of the results in Experiment 1, are in the case of the rib cuts, 1927 and 1957, but even here the changes are very slight and do not modify the conclusions previously made relating to the changes which took place in storage during the first 3 weeks. This close agreement was to be expected. Since the samples in this test lost almost no moisture during the 20-day period of storage, the subsequent corrections would be very slight and inappreciable. On the other hand, in Experiment 2, the data as given in Table III are quite different in several respects from those in Table II. In both cases, the chuck and loin cuts, there is, as formerly, a distinct gain of soluble dry substance, but it is

TABLE III.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH. FAT-FREE SUBSTANCE.

EXPERIMENT 1.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Same Water Content.)

Description of sample	Lean beef, round.		Lean beef, rib.		Lean beef, plate.		Lean beef, loin.		Average of (4).	Average of (4).
Laboratory No.	1924	1954	1927	1957	1929	1959	1926	1956		
Time held in cold storage (days)	2	22	2	22	2	22	2	22	2	22
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	76.32	76 32	76.71	76.71	76 53	76.53	76.32	76.32	76.49	76.49
Dry substance:										
Soluble	6.18	6.26	5.55	5.61	5.27	4.87	6.32	5.98	5.83	5.69
Insoluble	17.50	17 41	17.74	17.68	18.20	18.60	17.36	17.66	17.70	17.84
Total	*23 68*	*23.67*	*23.20*	*23.29*	*23.47*	*23.47*	*23.68*	*23.64*	*23.53*	*23.53*
Protein:										
Soluble coagulable	2.45	2.24	2.06	2.16	1.80	1.75	2.34	2.14	2.16	2.07
Soluble non-coagulable	0.16	0.27	0.21	0.31	0.21	0.25	0.24	0.25	0.21	0.27
Total	*2.61*	*2 51*	*2.27*	*2.47*	*2.01*	*2.00*	*2.58*	*2.39*	*2.37*	*2.34*
Insoluble	17.32	17.35	17.57	17.52	18.06	18.35	17.32	17.55	17.57	17.70
Total	*19.93*	*19.86*	*19.84*	*19.99*	*20.07*	*20.35*	*19.90*	*19.94*	*19.94*	*20.04*
Organic extractives:										
Nitrogenous	1.32	1.25	1.15	1.03	1.09	0.95	1.30	1.19	1.21	1.11
Non-nitrogenous	1.31	1.50	1.23	1.26	1.25	1.21	1.53	1.44	1.33	1.35
Total	*2.63*	*2.75*	*2.38*	*2.29*	*2.34*	*2.16*	*2.83*	*2.63*	*2.54*	*2.46*
Ash:										
Soluble	0.93	1.00	0.90	0.84	0.92	0.70	0.91	0.96	0.91	0.88
Insoluble	0.18	0.06	0.16	0.18	0.14	0.26	0.04	0.11	0.13	0.15
Total	*1.11*	*1.06*	*1.06*	*1.02*	*1.06*	*0.96*	*0.95*	*1.07*	*1.04*	*1.03*
Nitrogen:										
As soluble coagulable protein	0.392	0.357	0.330	0.347	0.289	0.281	0 373	0.343	0.346	0.332
As soluble non-coagulable protein	0.026	0.044	0.033	0.050	0.032	0.040	0.039	0.040	0.032	0.043
Total	*0.418*	*0.401*	*0.363*	*0.397*	*0.321*	*0.321*	*0.412*	*0.383*	*0.378*	*0.375*
As soluble non-protein substance	0.423	0.401	0.369	0.331	0.350	0.303	0.417	0.387	0.390	0.356
Total	*0.841*	*0.802*	*0.732*	*0.728*	*0.671*	*0.624*	*0.829*	*0.770*	*0.768*	*0.731*
Insoluble	2.771	2.776	2.812	2.800	2.889	2.935	2.771	2.806	2.811	2.829
Total	*3.612*	*3.578*	*3.544*	*3.528*	*3.560*	*3.559*	*3.600*	*3.576*	*3.579*	*3.560*
Ratio of non protein to protein:										
In water extract	1: 0.98	1: 1.00	1· 0.98	1. 1.20	1: 0.92	1: 1.06	1: 0.99	1: 0.99	1: 0.97	1: 1.06
In meats	1: 7 52	1: 7.92	1: 8.60	1: 9 67	1: 9.17	1: 10.74	1: 7.63	1: 8 24	1: 8.18	1: 9.01
Phosphorus:										
Soluble inorganic	0.104	0.129	0.113	0.121	0.097	0.123	0.109	0.125	0.106	0.124
Soluble organic	0.053	0.056	0.049	0.050	0.064	0.037	0.051	0.050	0.054	0.048
Total	*0.157*	*0.185*	*0.162*	*0.171*	*0.161*	*0.160*	*0.160*	*0.175*	*0.160*	*0.172*
Insoluble	0.088	0.060	0.064	0.053	0.066	0.056	0.082	0.069	0.075	0.061
Total	*0.245*	*0.245*	*0.226*	*0.224*	*0.227*	*0.216*	*0.242*	*0.244*	*0.235*	*0.233*

TABLE III.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH. FAT-FREE SUBSTANCE—(*Continued*).

EXPERIMENT 2.—LEAN OF WHOLESALE CUTS OF BEEF, UNCOOKED.

(Calculated to the Same Water Content.)

Description of sample	Lean beef, chuck.		Lean beef, loin.		Average of (2).	Average of (2).
Laboratory No.	1973	1993	1969	1988		
Time held in cold storage (days)	6	43	6	43	6	43
	P. ct	P. ct.	P. ct.	P. ct.	P. ct	P. ct.
Water	77.35	77.35	76.91	76.91	77.13	77.13
Dry substance:						
Soluble	5.30	5.68	5.97	6.59	5.63	6.13
Insoluble	17.35	16.97	17.12	16.50	17.23	16.74
Total	*22.65*	*22.65*	*23.09*	*23.09*	*22.87*	*22.87*
Protein:						
Soluble coagulable	1.84	2.09	2.20	2.18	2.02	2.13
Soluble non-coagulable	0.28	0.22	0.19	0.29	0.23	0.26
Total	*2.12*	*2.31*	*2.39*	*2.47*	*2.25*	*2.39*
Insoluble	17.13	16.74	16.97	16.52	17.05	16.53
Total	*19.25*	*19.05*	*19.36*	*18.79*	*19.30*	*18.92*
Organic extractives:						
Nitrogenous	0.98	1.05	1.10	1.29	1.04	1.17
Non-nitrogenous	1.35	1.58	1.56	1.93	1.45	1.75
Total	*2.33*	*2.63*	*2.66*	*3.22*	*2.49*	*2.92*
Ash:						
Soluble	0.85	0.74	0.92	0.90	0.89	0.82
Insoluble	0.22	0.23	0.15	0.18	0.18	0.20
Total	*1.07*	*0.97*	*1.07*	*1.08*	*1.07*	*1.02*
Nitrogen:						
As soluble coagulable protein	0.293	0.336	0.351	0.349	0.322	0.342
As soluble non-coagulable protein	0.046	0.036	0.032	0.046	0.039	0.041
Total	*0.339*	*0.372*	*0.383*	*0.395*	*0.361*	*0.383*
As soluble non-protein substance	0.312	0.332	0.356	0.414	0.334	0.373
Total	*0.651*	*0.704*	*0.739*	*0.809*	*0.695*	*0.756*
Insoluble	2.741	2.675	2.714	2.612	2.727	2.644
Total	*3.392*	*3.379*	*3.453*	*3.421*	*3.422*	*3.400*
Ratio of non-protein to protein:						
In water extract	1: 1.09	1: 1.12	1: 1.07	1: 0.95	1: 1.08	1: 1.02
In meats	1: 9.87	1: 9.17	1: 8.44	1: 7.24	1: 9.11	1: 8.09
Phosphorus:						
Soluble inorganic	0.106	0.128	0.109	0.137	0.107	0.132
Soluble organic	0.051	0.018	0.061	0.066	0.056	0.042
Total	*0.157*	*0.146*	*0.170*	*0.203*	*0.163*	*0.174*
Insoluble	0.076	0.087	0.090	0.017	0.082	0.052
Total	*0.233*	*0.233*	*0.260*	*0.220*	*0.245*	*0.226*

less, being, in per cent. of the totals in the 6-day samples, 8.9 per cent. against 13.8 per cent. The percentage of insoluble dry substance in Table III is less in the 43-day samples, whereas it was higher in Table II, being 0.49 per cent. in the former case and 0.26 in the second, which means a total loss of 2.8 per cent. on the one hand and a total gain of 1.5 on the other. Perhaps, the most important changes are in the proteins: the coagulable form shows nothing consistent, being higher in the chuck cut and lower in the loin cut; the non-coagulable is practically the same as in the former case; the total soluble and insoluble forms of protein show only a slight tendency to gain, while the total form is lower, whereas it was higher in Table II. As regards this last point, the average percentage loss of the insoluble and total protein are 3.0 and 2.0 respectively, whereas the average percentage loss and gain were 1.3 and 2.4 respectively in Table II. The percentages of the organic extractives still show the same general tendency to gain during the longer period of hanging in cold storage as in Table II, but to a lesser degree. The percentages of the nitrogenous forms represent a total gain of 12.5 per cent. now; while it was 17.3 per cent., the non-nitrogenous shows an increase of 20.7 per cent. against one of 26.9 per cent., and the total extractives a gain of 17.3 per cent. in Table III and of 22.9 per cent. in Table II. The total soluble nitrogen indicates an actual gain due to the hanging in cold storage of 8.8 per cent. against one of 13.9 per cent. when the loss of water was not taken into account. The insoluble nitrogen shows a loss of 3.0 per cent. under these conditions while it indicated a gain of 1.3 per cent. before. The total nitrogen in the 43-day samples was formerly 3.9 per cent. higher than that in the 6-day samples but now it is practically the same in both cases, being lower by 0.6 per cent. of the total amount for the 43-day meats. Concerning the soluble inorganic phosphorus, the data are higher in the meats kept in storage for the whole period, but like the organic

extractives the percentage gain is lower, being on the average 23.3, allowing for the loss of water, and 29.9, not taking this factor into account.

It is thus apparent that many of the changes which took place in the meats of Experiment 2 during cold storage were due to other causes than simply the loss of moisture. In the discussion, it has been evident that the loss of water produced a proportional increase in all the other constituents of the meats, but even allowing for this fact, the data show that other agencies such as enzymes and ferments were active in bringing about many of the intra-chemical changes which caused the so-called ripening of the meats. Among these changes, it may be stated in general that the meats became: (1) more easily soluble in cold water as is shown by the increase of 8.9 per cent. of the water-soluble dry substance; (2) slightly lower in their per cent. of insoluble and total protein, apparently resulting in a subsequent increase in the nitrogenous organic extractives, and hence in flavor; (3) higher in the percentage of non-nitrogenous organic extractives which indicates the possible formation of lactic acid and some other products from the cleavage of the insoluble protein into the non-protein form; (4) higher in the percentage of nitrogenous and total organic extractives, total soluble nitrogen, and soluble inorganic phosphorus; and (5) lower in the ratios of the soluble non-protein nitrogen to the total protein nitrogen.

In comparing the data throughout for the uncooked beef in Experiments 1 and 2, they indicate that the changes due to ripening which occurred during the hanging in cold storage apparently began in the first three weeks with an increase in the soluble inorganic phosphorus and its accompanying acidity, also with a decrease in the non-protein nitrogen and nitrogenous extractives and the total soluble nitrogen but with no changes in the percentage of protein; then, in the following three weeks, the meats did not increase appreciably in soluble inorganic phosphorus but rather in non-nitrogenous and nitrogenous organic extractives, in total soluble and non-protein nitrogen and in total soluble dry substance, while they decreased slightly in the insoluble and total protein, and also in the insoluble dry substance.

INFLUENCE OF COLD STORAGE UPON POULTRY.

The purpose and plan of this experiment, number 3, were given in detail on pages 418–19 and suffice it to repeat briefly that drawn and undrawn frozen chicken which were kept in cold storage for different lengths of time and fresh chicken were examined and studied in exactly the same manner as the uncooked beef which we have previously been considering. The several data are given in Tables IV, V, and VI calculated to the usual forms. It will be recalled that the lots of chicken represented by laboratory numbers 2067, 2111, and 2112 were all procured at the same time and placed under the supervision of one of us, while those for laboratory numbers 2057 and 2110 were gotten at different times, each being sent to the laboratory at our request by two large wholesale firms. In each case, in preparing the samples, the chicken were allowed to thaw in the ice box and were not put in water.

Fresh Substance.

The data of the edible lean meat, calculated to the fresh substance, show in exactly the same manner as did that of the beef—the great variations in the moisture and fat content. This is especially noticeable in the case of samples, laboratory numbers 2067 and 2111, where the percentage of water is 71.88 and 62.41, and that of fat is 6.41 and 18.15 respectively. The method of preparing the fowl for analysis might account in part for this variation in fat, since in each case all the lumps and layers of adipose tissue were carefully removed, but yet not in a quantitative manner. On the other hand, inasmuch as it seemed evident from the discussion upon beef that the variations in water content influenced the percentage of fat in a reciprocal manner, a fact which Wait[1] also found to be true, the loss of moisture during storage would seem to help account for the increased fat content.

In comparing the two 120-day frozen samples of chicken with the fresh sample, the loss in the moisture in the edible meat is quite distinct, being 9.47 per cent. in the undrawn and 6.27 per cent. in the drawn, averaging a loss of 7.87 per cent., which is five times as great as the loss of the 43-day refrigerated samples of beef. The fact that the flesh of the drawn chicken seems to contain more moisture than that of the undrawn samples cannot be taken up in this discussion until further investigations are made. It would seem perhaps that the greater exposure of surface in freezing and thawing might be a partial explanation. The percentages of fat in the samples 2067, 2111 and 2112 show that the frozen stored fowl contain on an average 16.58 per cent. while fresh chicken

[1] *U. S. Dept. of Agr., Office of Experiment Stations, Bull.* 53.

contains 6.41 per cent., a difference of 10.17 per cent. The influence of this fact is also brought out in the amounts of insoluble and total dry substance, which are respectively 8.90 and 8.44 per cent. higher, for the cold storage fowl. It is significant to note that the forms of protein are all lower in the frozen chicken, being 0.21, 0.03 0.24, 1.21, and 1.44 per cent. for the coagulable, non-coagulable, total soluble, the insoluble, and total protein, meaning a percentage decrease of 16.0, 21.0, 16.4, 7.2, and 7.9 respectively. The percentage of total soluble and total nitrogen are also lower in the cold storage samples, being 0.104 per cent. for the former and 0.295 per cent. for the latter, and making a percentage difference of 17.4 and 9.0. As regards the organic extractives, the non-nitrogenous form is practically the same, the nitrogenous form is 16.9 per cent. lower and the total is 7.4 per cent. lower. The ash shows a decrease in each form.

In studying the composition of the other two samples of frozen chicken, it is evident that nothing of a comparative nature can be ascertained as to the changes taking place in storage since the samples were procured and prepared at different times, kept in storage for unequal lengths of time, and were in themselves from different lots of chickens. However, these data show the interesting fact that they are not unlike the other three samples in regard to their nutritive value. This will become much more evident in discussing these data calculated to the fat-free basis and later to the same water content. It is of importance to note in passing that the percentage of non-coagulable protein, which includes the albumoses, is practically the same in the 630-day frozen and the fresh samples of chicken, although the percentage of total soluble protein is higher in the former case.

The results of the analyses of the poultry calculated to the fat-free basis are given in the following table, No. V.

TABLE IV. CHEMICAL COMPOSITION OF COLD STORAGE FLESH.
EXPERIMENT 3. EDIBLE PORTION OF FROZEN CHICKEN.
(Calculated to Fresh Substance.)

Description of sample	Fresh chicken.	Frozen chicken. Undrawn.	Drawn.	Undrawn.	Drawn.
Laboratory No.	2067	2111	2112	2057	2110
Time held in cold storage (days)	0	120	120	630	?
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	71.88	62.41	65.61	73.12	67.42
Dry substance:					
Soluble	4.48	4.11	3.95	5.65	5.67
Insoluble	23.30	33.90	30.49	21.62	27.38
Total	*27.78*	*38.01*	*34.44*	*27.27*	*33.05*
Protein:					
Soluble coagulable	1.32	1.04	1.18	2.09	1.91
Soluble non-coagulable	0.14	0.11	0.11	0.19	0.26
Total	*1.46*	*1.15*	*1.29*	*2.28*	*2.17*
Insoluble	16.68	15.66	15.29	16.26	16.81
Total	*18.14*	*16.81*	*16.58*	*18.54*	*18.98*
Organic extractives:					
Nitrogenous	1.13	0.91	0.96	1.22	1.24
Non-nitrogenous	1.15	1.31	1.05	1.36	1.50
Total	*2.28*	*2.22*	*2.01*	*2.58*	*2.74*
Fat	6.41	18.15	15.02	5.15	10.44
Ash:					
Soluble	0.74	0.74	0.65	0.79	0.76
Insoluble	0.21	0.09	0.18	0.21	0.13
Total	*0.95*	*0.83*	*0.83*	*1.00*	*0.89*
Nitrogen:					
As soluble coagulable protein	0.212	0.167	0.189	0.334	0.306
As soluble non-coagulable protein	0.022	0.016	0.017	0.030	0.040
Total	*0.234*	*0.183*	*0.206*	*0.364*	*0.346*
As soluble non-protein substance	0.363	0.292	0.306	0.390	0.396
Total	*0.597*	*0.475*	*0.512*	*0.754*	*0.742*
Insoluble	2.668	2.506	2.447	2.602	2.691
Total	*3.265*	*2 981*	*2.959*	*3.356*	*3.433*
Phosphorus:					
Soluble inorganic	......	0.113	0.108	......	0.118
Soluble organic	......	0.018	0.022	......	0.017
Total	......	*0.131*	*0.130*	......	*0.135*
Insoluble	......	0.047	0.050	......	0.044
Total	......	*0.178*	*0.180*	......	*0 179*

Fat-free Substance.

It will now be of interest to consider these data calculated to the fat-free basis. Comparing the three samples, numbers 2067, 2111, and 2112, it

will be seen that there is very little difference in the moisture content in contrast to that found for the data calculated to the fresh substance. The percentage of water in the drawn frozen fowl, 2112, is practically the same as the fresh chicken, being 77.16 and 77.08 respectively. The undrawn fowl, 2111, has a percentage of moisture which is 1.22 per cent. lower than that of the fresh sample, and in turn this influences the percentage of insoluble and total dry substance and the insoluble and total protein, making them correspondingly higher. The percentage of the various constituents in the fresh and drawn fowl will be seen to be so close throughout that it is almost impossible to make any distinction between them. In view of this fact, it will be of interest to note the effect of calculating the composition of the undrawn fowl to the same water content as the fresh chicken and thus eliminate any of the differences which might be due to moisture. Under the present condition, the different forms of protein and nitrogen in the undrawn samples show the coagulable and total soluble forms to be slightly lower, the non-coagulable to be about the same, and the insoluble and total to be higher than those in the fresh sample. This fact shows again the effect of the influence of calculating the result to the fat-free basis, for upon the fresh basis, each form was distinctly lower in the frozen samples. The data for the other two samples of chicken, 2057 and 2110, show that they are just as nutritious as the first three. However, a direct comparison can best be made when they are all calculated to the same moisture content from the fat-free substance.

TABLE V.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH.

EXPERIMENT 3.—EDIBLE PORTION OF UNCOOKED FROZEN CHICKEN.

(Calculated to the Fat-free Basis.)

Description of sample	Fresh chicken.	Frozen chicken. Undrawn.	Drawn.	Undrawn.	Drawn.
Laboratory No.	2067	2111	2112	2057	2110
Time held in cold storage (days)	0	120	120	630	?
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	77.08	75.86	77.16	76.77	74.88
Dry substance:					
Soluble	4.80	5.00	4.65	5.93	6.30
Insoluble	18.12	19.14	18.19	17.29	18.82
Total	*22.92*	*24.14*	*22.84*	*23.22*	*25.12*
Protein:					
Soluble coagulable	1.41	1.26	1.39	2.19	2.12
Soluble non-coagulable	0.15	0.13	0.13	0.20	0.29
Total	*1.56*	*1.39*	*1.52*	*2.39*	*2.41*
Insoluble	17.89	19.04	17.98	17.07	18.67
Total	*19.45*	*20.43*	*19.50*	*19.46*	*21.08*
Organic extractives:					
Nitrogenous	1.21	1.11	1.13	1.28	1.38
Non-nitrogenous	1.23	1.59	1.23	1.43	1.66
Total	*2.44*	*2.70*	*2.36*	*2.71*	*3.04*
Ash:					
Soluble	0.79	0.90	0.76	0.83	0.84
Insoluble	0.23	0.11	0.21	0.22	0.15
Total	*1.02*	*1.01*	*0.97*	*1.05*	*0.99*
Nitrogen:					
As soluble coagulable protein	0.227	0.203	0.222	0.351	0.340
As soluble non-coagulable protein	0.024	0.019	0.020	0.031	0.044
Total	*0.251*	*0.222*	*0.242*	*0.382*	*0.384*
As soluble non-protein substance	0.389	0.355	0.360	0.410	0.440
Total	*0.640*	*0.577*	*0.602*	*0.792*	*0.824*
Insoluble	2.861	3.046	2.878	2.732	2.989
Total	*3.501*	*3.623*	*3.480*	*3.524*	*3.813*
Ratio of non-protein to protein:					
In water extract	1:0.64	1:0.63	1:0.67	1:0.93	1:0.87
In meats	1:8.00	1:9.21	1:8.67	1:7.59	1:7.67
Phosphorus:					
Soluble inorganic	......	0.137	0.127	......	0.131
Soluble organic	......	0.022	0.026	......	0.019
Total	......	*0.159*	*0.153*	......	*0.150*
Insoluble	......	0.057	0.059	......	0.049
Total	......	*0.216*	*0.212*	......	*0.199*

Fat-free Substance, Calculated to the Same Water Content.

In calculating these data to the same water content as that of the fresh unstored chicken, the results are in a condition which eliminates, as much as it is possible, the effect of desiccation during storage, and brings them to a form which makes a direct comparison more logical in so far as a

study of the actual changes taking place during storage, other than drying, are concerned.

Comparing the composition of the samples of the undrawn and drawn flesh, numbers 2111 and 2112, the data show that the two samples are very much alike in the percentage of the various constituents. This is especially true of the water-soluble and insoluble dry substance; the non-coagulable, insoluble and total protein; the nitrogenous extractives, the total ash; the non-coagulable, insoluble and total nitrogen and the various forms of phosphorus. There is a tendency for the non-nitrogenous and total extractives and the soluble ash to be lower, and also a tendency for the coagulable protein, the insoluble ash and the total soluble nitrogen to be higher in the sample from the drawn fowl. However, these differences are slight and of such a nature that they show that no radical changes have taken place in either of the samples to the extent of affecting their nutritive value. In the drawn poultry, the coagulable and water-soluble protein are higher, and in the undrawn poultry, the non-nitrogenous and total extractives are higher.

If these two sets of data be compared with the one for the fresh unstored sample, it will be seen, on taking their average, that they are almost the same throughout. Further, of the two samples of stored flesh, the drawn and undrawn, the composition of the former approaches more nearly to that of the fresh unstored sample. So closely do these three samples agree in their respective percentage chemical composition, that it may be stated from these data, first, that there is no difference in the nutritive value between the flesh from drawn and undrawn fowl which has been kept in storage 120 days, and second, that the flesh from drawn and undrawn frozen fowl which has been held in cold storage for 4 months show that the chemical changes are exceedingly few and of such a nature as to indicate

TABLE VI.—CHEMICAL COMPOSITION OF COLD STORAGE FLESH.

EXPERIMENT 3.—EDIBLE PORTION OF UNCOOKED FROZEN CHICKEN.

(Calculated to the Same Water Content.)

Description of sample	Fresh chicken.	Frozen chicken. Undrawn.	Frozen chicken. Drawn.	Frozen chicken. Undrawn.	Frozen chicken. Drawn.	Average of (2). Undrawn.	Average of (2). Drawn.
Laboratory No.	2067	2111	2112	2057	2110		
Time held in cold storage (days)	0	120	120	630	?		
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	77.08	77.08	77.08	77.08	77.08	77.08	77.08
Dry substance:							
Soluble	4.80	4.75	4.67	5.85	5.75	5.30	5.21
Insoluble	18.12	18.17	18.25	17.07	17.17	17.62	17.71
Total	*22.92*	*22.92*	*22.92*	*22.92*	*22.92*	*22.92*	*22.92*
Protein:							
Soluble coagulable	1.41	1.20	1.39	2.16	1.93	1.68	1.66
Soluble non-coagulable	0.15	0.12	0.13	0.20	0.27	0.16	0.20
Total	*1.56*	*1.32*	*1.52*	*2.36*	*2.20*	*1.84*	*1.86*
Insoluble	17.89	18.08	18.04	16.84	17.04	17.46	17.54
Total	*19.45*	*19.40*	*19.57*	*19.20*	*19.24*	*19.30*	*19.40*
Organic extractives:							
Nitrogenous	1.21	1.05	1.13	1.26	1.26	1.15	1.21
Non-nitrogenous	1.23	1.51	1.24	1.41	1.51	1.46	1.36
Total	*2.44*	*2.56*	*2.37*	*2.07*	*2.77*	*2.61*	*2.57*
Ash:							
Soluble	0.79	0.86	0.76	0.82	0.77	0.84	0.76
Insoluble	0.23	0.10	0.21	0.22	0.13	0.16	0.17
Total	*1.02*	*0.96*	*0.97*	*1.04*	*0.90*	*1.00*	*0.93*
Nitrogen:							
As soluble coagulable protein	0.227	0.193	0.223	0.346	0.310	0.269	0.266
As soluble non-coagulable protein	0.024	0.018	0.020	0.031	0.040	0.025	0.030
Total	*0.251*	*0.211*	*0.243*	*0.377*	*0.350*	*0.294*	*0.296*
As soluble non-protein substance	0.389	0.337	0.361	0.404	0.402	0.370	0.382
Total	*0.640*	*0.548*	*0.604*	*0.781*	*0.752*	*0.664*	*0.678*
Insoluble	2.861	2.892	2.888	2.696	2.727	2.794	2.807
Total	*3.501*	*3.440*	*3.492*	*3.477*	*3.479*	*3.458*	*3.485*
Ratio of non-protein to protein:							
In water extract	1:0.64	1:0.63	1:0.67	1:0.93	1:0.87	1:0.78	1:0.77
In meats	1:8.00	1:7.21	1:8.67	1:7.59	1:7.67	1:8.40	1:8.17
Phosphorus:							
Soluble inorganic	....	0.130	0.127	....	0.120	0.130	0.123
Soluble organic	....	0.021	0.026	....	0.017	0.021	0.022
Total	....	*0.151*	*0.153*	....	*0.137*	*0.151*	*0.145*
Insoluble	....	0.054	0.059	....	0.045	0.054	0.052
Total	....	*0.205*	*0.212*	....	*0.182*	*0.205*	*0.197*

that they do not affect the nutritive value of the flesh.

In considering the data for the other two samples, 2057 (undrawn) and 2110 (drawn), they will be found, when calculated to the same water content as that of the fresh unstored fowl, to be of very nearly the same composition for each constituent, and it is interesting to note that, contrary to the other two samples of drawn and undrawn chicken flesh, the percentages of coagulable and soluble protein, and of non-nitrogenous and total extractives vary in a reciprocal manner, the protein in this case being higher in the undrawn sample, and the extractives being lower. If the respective two samples of drawn and undrawn flesh be averaged, it will be seen that they are remarkably close in their percentage chemical composition, and again bring out the fact that there is no difference in the nutritive value of the two kinds of flesh, judging from their chemical composition.

Finally, a comparison of the composition of the lean of the fresh fowl with that of the other two samples of stored chicken will be of value. While such a comparison cannot be made upon the basis that all three are from the same original lot, yet a general idea can be had as to the nutritive value of each. The data show that the stored samples are quite like those of the fresh sample, showing the greatest difference in having a higher percentage of water-soluble dry substance, of coagulable, non-coagulable and total soluble protein; and a correspondingly lower percentage of insoluble dry substance and insoluble protein. The percentage total protein of the various extractives, of the forms of ash, and of the total nitrogen are very nearly the same. From these statements it is evident that the flesh from the chicken, which was kept in storage in one case as long as 630 days, is equally as nutritious as that of the fresh poultry.

CONCLUSIONS.

In making a comparison of the chemical composition of fresh and cold storage flesh, the samples of which were procured under known conditions and either from the same animal or the same lot of animals, it was found:

1. The method, as used in this laboratory, was sufficiently accurate to detect changes which occurred in flesh during cold storage.

2. In the case of the refrigerated beef which was stored for 22 days, the averaged data indicate:

(*a*) That there was no loss of water.

(*b*) That the percentage of the water-soluble solids, the soluble, insoluble and total protein, the non-coagulable protein, the nitrogenous and total organic extractives, the forms of ash, the total nitrogen and the total phosphorus, all remained practically unchanged.

(*c*) That the only consistent real changes were a distinct increase in the total soluble and the soluble inorganic phosphorus, being 8.0 and 17.9 per cent. respectively, and a decrease of 8.3 per cent. in the non-nitrogenous organic extractives.

(*d*) That the nutritive value of the meat was unaltered.

3. In the case of the refrigerated beef which was stored for 43 days, the averaged data show:

(*a*) That there was a loss of water amounting to 1.3 per cent.

(*b*) That this loss of water, causing a proportional increase in all the other constituents, produced differences in some instances which were sufficient to overbalance the amounts in the fresh samples.

(*c*) That the ratio of the non-protein to the protein nitrogen in the meats was lower.

(*d*) That when allowance was made for the loss of moisture, the additional changes which occurred in cold storage consisted in a definite increase in the soluble dry substance, the nitrogenous, non-nitrogenous, and total organic extractives, the total soluble nitrogen, the soluble inorganic phosphorus, and a slight increase in the soluble coagulable and total soluble protein nitrogen, and also in the insoluble and total nitrogen.

(*e*) That the chemical changes in the 43-day refrigerated meats were greater in number than in the 22-day samples yet as far as nutritive value was concerned, the former showed an increase in the organic extractives and soluble protein, and but an insignificant decrease in the total protein.

4. The analyses of the frozen drawn and undrawn chicken showed, when allowances were made for the variations in fat and moisture, that there was almost no difference between the two, one being equally as good as the other.

5. The analyses of the fresh and the frozen drawn and undrawn fowl, obtained from the same lot, showed that the latter changed but slightly and to such an extent that there was practically no difference in the nutritive value of the three, after correcting for the differences in the fat and moisture content.

The authors wish to acknowledge the assistance of Messrs. J. M. Barnhart and L. F. Shackell in

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The Laboratory of Physiological Chemistry,
Department of Animal Husbandry,
University of Illinois,
Urbana.

(Contribution from Division of Foods, Bureau of Chemistry, U. S. Department of Agriculture.)

COMPOSITION OF SCUPPERNONG, CONCORD, AND CATAWBA GRAPE JUICES, WITH SOME NOTES ON THE DETERMINATION OF TOTAL ACID.[1]

By H. C. Gore.

Received March 25, 1909.

The use of unfermented grape juice is increasing, and fairly complete analyses of juices prepared from American varieties of grapes will probably be of interest to many. The juices considered here differ from the fresh musts in that they have been sterilized by heat and allowed to stand for at least several weeks before analyzing. During this time considerable quantities of sediment were usually deposited consisting largely of crystals of potassium bi-tartrate. The supernatant liquor constitutes the grape juice. This method of allowing the juice to stand after having been sterilized, then racking off, is followed in the preparation of grape juice on a commercial scale.

All samples have been prepared by the writer or under his immediate direction and on as large a scale as practicable, so that the results might be strictly comparable with those which would be obtained under commercial conditions. In all cases at least 200 pounds of grapes were employed. In the case of Catawba grape juice several tons of grapes were used, and although one analysis only of Catawba juice is given, the sample is probably thoroughly representative of the Catawba juice of this year in the Northern Ohio grape district. A statement of the general character of the three varieties of grapes as furnished by Mr. Geo. C. Husmann, Pomologist in charge of Viticultural Investigations of this Department, is given below.

Scuppernong.—A variety of the Rotundifolia species. The designation "Scuppernong" is at present usually applied to all the lighter colored varieties of the Rotundifolia species and often even to the entire species. It is esteemed for its eating and wine-making qualities. Bunch of from six to twelve berries; berries large, thick skin, pulpy, fairly sweet, sprightly with a musky scent and flavor. It is esteemed by some, repugnant to others. Very vigorous and productive in the South Atlantic and Gulf states.

Mish.—A variety of the Rotundifolia species. Supposed to have been discovered by Mr. Albert Mish near the middle of the last century in the vicinity of Washington, N. C. It is at present one of the most extensively grown of the dark colored varieties of this species. Bunches small and straggling; berries ovoid, juicy; flavor delicious and distinct; skin black, with numerous lighter colored specks. One of the best of the dark Rotundifolias for wine purposes. Very productive.

James.—Variety of the Rotundifolia species. It was discovered by Mr. B. M. W. James, of Grindool, N. C., about 1866 near Grindool Creek, Grindool Post Office. Bunch, like all Rotundifolias, small and rather loose. Berries large, showy, round, juicy, slightly pulpy, sprightly, with the peculiar flavor of the Rotundifolia. Very prolific. It is one of the most extensively grown of the dark varieties.

Concord.—A variety of the Labrusca species. It originated with Mr. E. W. Bull, of Concord, Mass. He exhibited it for the first time in September, 1853. Bunch above medium size, globular, black, thickly covered with beautiful blue bloom; skin moderately thin, tender, cracks easily; flesh moderately sweet, pulpy, tender. Time of ripening medium to late. Fruit of fair keeping quality, becoming insipid soon after being gathered. More fruit of this variety is sold as a table grape in our markets than of all other American varieties combined. At least 75 per cent. of the unfermented grape juice made from native species is of this variety. It makes a light red wine of fair quality and a white wine can also be made by pressing the grapes immediately after they are crushed. This is unquestionably the best known and most extensively grown variety of our native species.

Catawba.—A variety of the Labrusca species. Native of North Carolina and has its name from the Catawba River. Introduced to notice by Major John Adlum, Georgetown, D. C., in 1825. It was for many years the standard wine grape of the country. On account of it being very subject to mildew, black rot and a so-called blight, and its late ripening in the northern and northeastern states it is not so much grown now as formerly. Bunch medium size, fairly compact, shouldered. Berries medium size, round, deep red, covered with lilac bloom; skin moderately thick, flesh slightly pulpy, sweet and juicy with a rich vinous somewhat

[1] Published by permission of the Secretary of Agriculture.

musky flavor, a good grower, and in favorable seasons and localities productive.

This year (1908) was a favorable one for the development of sugar in grapes in the localities from which the fruit was obtained. This fact must be taken into account in comparing these analyses with others which may be made in other years. All grapes employed were sound and fully ripe. The Scuppernong varieties were obtained from the Medoc vineyards at Enfield, North Carolina. A small proportion of these grapes showed the peculiar mellowness or softening of the pulp which occurs in this species after picking. The Concord grapes were obtained late in the season at the local market and came from the Keuka Lake region, New York. They were very ripe, but entirely sound and of excellent quality. The Catawba grapes were grown near Danbury in Northern Ohio. They were well colored and flavored. This fruit was ground, stemmed and pressed in a winery at Sandusky, Ohio.

The methods of analysis employed were those of the Association of Official Agricultural Chemists[1] with the exceptions as noted below. The specific gravity was determined with a Brix spindle which when checked with a pycnometer was found to give correct results. The readings were taken at 20° C. and corrected to 17.5° C. The alkalinity of the ash was determined by extracting the ash on a filter with hot water and titrating as directed. For phosphoric acid the ash was moistened with nitric acid, taken up with water, and finished by the official method. Digestion by the Neumann[2] method with nitric and sulphuric acids which has been shown by LeClerc and Leavitt[3] to be necessary in case of the ash of wheat, was found not to be required in case of the ash of these juices.

Total acid was determined by titrating 10 cc. samples, using litmus as indicator. A discussion of the method comprises the latter portion of this paper. Total tartrates were run by the official method, employing a modification necessitated by the viscous nature of the cooked Concord juice, which probably contains a considerable amount of pectin formed from the disintegrating pulp cells during the heating. When alcohol is added as required in the method, a slimy precipitate forms, making it impossible to use a Gooch filter as directed. A four-inch Büchner funnel was substituted, using nine cm. filter papers. This was

TABLE I.—ANALYSES OF GRAPE JUICES.

Variety.	Description	Sediment strain interval days.	Corrected Brix reading.	Specific gravity from Brix reading.	Ash.	Alkalinity of ash as K_2CO_3. Per cent.	Total phosphoric acid, P_2O_5. Per cent.	Total acid as tartaric. Per cent.	Total tartrates as tartaric acid. Per cent.	Protein N 6¼. Per cent.	Reducing sugar as invert. Per cent.	Total sugar as invert. Per cent.	Polarization at 20° C. Normal weight in 200 mm. tube. Direct. Per cent.	Polarization at 20° C. Normal weight in 200 mm. tube. Invert. Per cent.	Sucrose by reduction. Per cent.	Sucrose by polarization. Per cent.	Tannin and coloring matter. Per cent.	Undetermined solids. Per cent.
Scuppernong	Cold pressed, very pale yellow	75	14.77	1.0603	0.16	0.11	0.015	0.72	0.45	0.07	13.42	13.49	—4.65	—5.10	0.07	0.34	0.026	0.30
Mish	Cold pressed, pale yellow	61	16.57	1.0681	0.22	0.16	0.014	0.81	0.53	0.14	12.88	14.88	—2.05	—4.60	1.90	1.85	0.027	0.49
James	Cold pressed, light red	61	13.47	1.0547	0.19	0.12	0.012	0.44	0.30	0.07	12.33	12.13	—4.65	—4.65	none	none	0.035	0.40
Concord	Cold pressed, dark red	31	20.37	1.0849	0.27	0.19	0.026	0.68	0.56	0.30	18.60	18.34	—7.7	—7.8	none	0.10	0.056	0.46
Concord	Cold pressed, dark red	23	19.97	1.0831	0.29	0.19	0.031	0.78	0.60	0.27	17.89	17.77	—7.7	—7.6	none	none	0.058	0.68
Concord	Cold pressed, dark red, macerated 16 hours	30	19.27	1.0800	0.32	0.22	0.031	0.82	0.61	0.39	17.04	16.86	—6.7	—7.35	none	0.47	0.070	0.63
Concord	Hot pressed, very dark red, unstemmed	31	22.07	1.0926	0.32	0.22	0.046	0.89	0.68	0.42	18.60	18.40	—7.5	—7.5	none	none	0.402	1.44
Concord	Hot pressed, very dark red, stemmed	31	20.67	1.0864	0.29	0.21	0.037	0.86	0.70	0.45	17.85	17.35	—7.15	—6.8	none	none	0.363	0.86
Concord	Hot pressed, very dark red, stemmed	23	22.17	1.0931	0.32	0.21	0.048	1.02	0.71	0.41	18.95	18.69	—7.5	—7.6	none	0.10	0.437	1.03
Catawba	Cold pressed, light brownish yellow	41	20.07	1.0836	0.27	0.17	0.026	0.93	0.67	0.42	17.98	17.74	—7.1	—7.2	none	0.10	0.061	0.41

[1] *U. S. Dept. Agr., Bur. Chem., Bull.* **107**, revised.
[2] *Zeit. physiol. Chem.*, **37**, 115.
[3] *J. Am. Chem. Soc.*, **30**, 391 and 617.

found much more convenient to use than the Gooch crucible, and its use can introduce no appreciable error. When working with cooked Concord juice it was found advisable to throw the alcoholic precipitate which floats on the surface on to the filter paper first. This is sucked as dry as possible, and washed with small portions of the washing mixture. This paper is then removed, a fresh paper substituted, and the main crop of crystals collected.

Beaker and precipitate are well rinsed with successive small portions of washing mixture, both papers returned to the beaker, and the determination finished as usual.

Total nitrogen was determined by the Nitrogen Laboratory of this Bureau. Sugars were estimated, using the method of Munson and Walker.[1] The juices were clarified for sugar determination by first adding calcium carbonate, then solution of neutral lead acetate, making up to volume, filtering, precipitating excess of lead acetate with dry potassium oxalate and again filtering. The undetermined matter shown in the table is the total solids (corrected Brix reading) less the sum of the ash, acid, protein, sugar, and tannin and coloring matter.

An inspection of the results indicates that the Scuppernong juices are considerably less rich than the other varieties in sugar, ash, alkalinity of ash, phosphoric acid, total tartrates calculated as tartaric acid, protein, and tannin and coloring matter. A unique feature of these juices is the fact that they contain sucrose even after standing for weeks. In the case of Mish juice nearly two per cent. of cane sugar was found by reduction and polarization methods and more undoubtedly existed in the juice as it came from the press. The Scuppernong grape juice was shown to contain cane sugar and its presence was verified by a special determination made by Dr. C. S. Hudson, of this Bureau, on the day that the juice was pressed. According to his observations, inverting by use of invertase, 0.69 per cent. of sucrose was present.

Three lots of the Concord grapes were pressed without previous heating and three lots were heated before pressing by bringing to the boiling-point with constant stirring in a steam-jacketed kettle. One of the cold-pressed samples was allowed to stand after crushing for a period of 16 hours to determine what effect, if any, would be produced. The effect of this maceration seems to consist in a slight lowering of the specific gravity of the juice, a slight increase in nitrogen, and a decrease in the sugar. Fermentation had not started as a special determination showed the absence of alcohol.

In the case of the hot-pressed Concord juices a contrast is shown between juices prepared from the stemmed and the unstemmed grapes pressed on the same day. The juice of the unstemmed grapes is higher in solids, ash, phosphoric acid and sugar than that from the stemmed grapes. It is also higher in tannin. These differences, may, however, be due to slight differences in the heat treatment.

Comparing the cold- and hot-pressed juices it will be noted that there is a considerable increase in the solids of the hot-pressed juices and that this increase is not due to increase in sugar but is due to a slight increase in ash, total acid, and total tartrates, an increase in nitrogen, and a decided increase in undetermined solids, and tannin and coloring matter.

The Catawba grape juice is similar in composition to the cold-pressed Concord juice but higher in total acids, total tartrates and protein.

NOTES ON THE DETERMINATION OF TOTAL ACID.

Results obtained by Hortvet[1] have led him to regard phenolphthalein as far superior to litmus as an indicator for the commonly occurring organic acids of wines. Working with the pure acids not only did he find the end point to be unsatisfactory with litmus, but that only 90 to 95 per cent. of various acids were titrated, while with phenolphthalein the end point was sharp and practically 100 per cent. was found. That the latter indicator is most suitable when the organic acids are not associated with coloring matter, is generally recognized, but if, as Hortvet states, it is greatly superior for general use, it is quite remarkable that litmus is still retained. The difficulties in using phenolphthalein with colored products appear to be well recognized. Litmus is preferred by Windisch[2] in the titration of wines and by Schüle[3] in case of strongly colored distilled liquors and vinegars.

The grape juices analyzed above afforded a good opportunity for studying the action of the two indicators in the determination of total acid.

[1] *U. S. Dept. Agr., Bull* **107**, revised, and *J. Am. Chem. Soc.*, **28**, 663.

[1] "The Determination of Total, Fixed and Volatile Acid in Wines," THIS JOURNAL, **1**, 31.

[2] Lunge, *Chem Techn. Unters. Meth.*, 5th ed., Vol. 3, p. 606.

[3] *Ibid.*, pp. 566 and 590.

Titrations of dilute solutions of organic acids have also been made. The litmus used was purified by one of the methods found in the standard textbooks which direct the removal of the coloring matters other than the azolitmus by extraction with hot alcohol. In titrating, a dilute solution of litmus of neutral tint was placed in small drops on a white glass plate and was thus used as an outside indicator. This method, including the precaution of employing a litmus which has been thoroughly extracted with hot alcohol, is due to Mr. C. S. Ash,[1] chemist of the California Wine Association. In titrating a dilute solution of an organic acid, the end point is essentially the same as when the indicator is used inside. In the titration of a colored grape juice the end point is satisfactory and much sharper than by either using litmus inside or outside on paper. After exposure to the air for a few moments on the white plate the drops of neutral tinted litmus become blue, and very slight amounts of free acid in the drops of the solution being titrated are easily detected by the reddish tinge imparted. If the sample is greatly diluted—say one part of the juice to forty parts of water—somewhat low results may be expected, but there will probably be found no occasion for great dilutions as it is found that the natural colors even of the very dark, hot-pressed Concord juices, do not interfere with the sharpness of the end point, duplicates agreeing usually within 0.1 cc.

[1] Verbally communicated.

To understand the difficulties of using phenolphthalein as an indicator in colored grape juices it is necessary to consider the color changes which ensue as such a juice is gradually made alkaline. With a cold-pressed Concord juice, for example, working under the conditions mentioned below, the red color gradually fades and, as ordinarily viewed by reflected light, entirely disappears shortly before the point where the juice is neutral to litmus. After this neutral point is reached, if a few tenths of a cc. of alkali are added, a green color develops which up to now has been observed during the titration where there has existed in the solution a momentary local excess of alkali. If more alkali is added the green color deepens, soon approaching a maximum. Viewed by transmitted light, this green is found to be mixed with a red whose presence is readily verified by viewing the solution through a direct vision spectroscope.

If phenolphthalein is present its effect at the time the end point for this indicator is reached, is slightly to change the shade of the solution. This occurs just after the green begins to develop. As the titration progresses from the point where the green color first appears, the green deepens and at the same time the red, due to the phenolphthalein, begins to develop and it is impossible to detect with certainty at just what point a change in color, due to phenolphthalein, occurs unless the somewhat cumbersome device is employed of titrating a blank, that is, a grape juice solution to which no indicator has been added, side by side with the

TABLE II.—SHOWING THE RESULTS OF TITRATION OF ORGANIC ACIDS, USING LITMUS AND PHENOLPHTHALEIN.

Acid.	Description.	Concentration.	Used for titration, cc.	Tenth-normal soda required: using litmus, cc.	Tenth-normal soda required: using phenolphthalein, cc.	Differences, cc.	Per cent of acid indicated by litmus.
Tartaric	B. & L. C. P.	0.5 gr. in 100 cc	10	6.45	6.65	0.2	97
"	"	" " "	20	13.0	13.4	0.4	97
"	"	" " "	20	13.0	13.4	0.4	97
"	"	1.0 gr. in 100 cc	10	12.95	13.35	0.4	97
Potassium bitartrate	"	" " "	10	5.1	5.2	0.1	98
" "	"	" " "	10	5.0	5.3	0.3	94
" "	"	" " "	20	10.4	10.6	0.2	98
Acetic	"	0.5 gr. " "	10	16.25	16.45	0.2	99
"	"	" " "	10	16.30	16.4	0.1	99
"	"	" " "	20	33.3	33.6	0.3	99
"	"	" " "	20	32.4	32.75	0.35	99
Lactic	"	1.0 gr " "	10	7.9	8.1	0.2	98
"	"	" " "	20	15.8	16.3	0.5	97
"	"	" " "	20	15.9	16.25	0.35	98
Malic	Merck's C. P.	" " "	10	14.8	15.0	0.2	99
"	"	" " "	10	14.85	14.95	0.1	99
Citric	B. & L. non-hydrated	1.0 gr. in 100 cc.	10	14.25	14.2	0.05	100.4
"	"	" " "	10	14.2	14.2	0.0	100.0
"	"	" " "	20	28.65	28.55	0.10	100.3
Succinic	E. & A. C. P.	" " "	10	16.75	16.9	0.15	99
"	"	" " "	20	33.80	33.9	0.1	99
Benzoic	Merck's C. P.	" " 1000 cc.	100	7.9	8.15	0.25	97
"	"	" " "	100	8.0	8.2	0.2	98

solution containing phenolphthalein, using another burette. The slight amount of red naturally occurring in the neutralized or alkaline grape juice probably renders the change in shade due to slight amounts of phenolphthalein red still more difficult to recognize. By titrating a blank simultaneously, however, adding exactly the same amount of alkali as employed in titrating the solution when phenolphthalein is used, the true end point may be found quite as sharply as could be desired. This method was followed with the titrations of grape juices given below except in case of the Scuppernong and Mish juices, which were practically free from coloring matter.

from 96 to 98 per cent. of the acids were indicated by litmus. These juices were low in tannin and coloring matter, and after treatment with carbon black, which was found to remove a considerable proportion of the acid as well as the tannin and color, practically the same percentages of the organic acids were titrated as before.

The end points indicated by litmus and phenolphthalein were found to be wide apart in the titrations of the hot-pressed Concord juices which were rich in tannin and coloring matter. Apparently only from 85 to 90 per cent. of the organic acids are indicated by litmus. When decolorized by carbon black the end points were very much nearer

Table III.—Showing the Results of Titrating Grape Juices, Using Litmus and Phenolphthalein.

		Before treating with carbon black.				Color removed by carbon black.[1]			
		Tenth-normal soda required				Tenth-normal soda required			
Variety	Description	using litmus, cc.	using phenolphthalein, cc.	Differences, cc.	Per cent. of acid indicated by litmus.	using litmus, cc.	using phenolphthalein, cc.	Differences, cc.	Per cent. of acid indicated by litmus.
Scuppernong	Cold pressed	9.6	9.9	0.3	97	9.15	9.4	0.25	97
"	"	.....	.....	....	..	9.05	9.35	0.3	97
Mish	"	10.8	11.15	0.35	97	10.65	11.05	0.4	96
"	"	.....	.....	....	..	.....	.....	....	..
James	.....	5.8	5.95	0.15	97	5.15	5.4	0.35	95
"	"	.....	.....	....	..	5 2	.....	....	..
Concord	"	9.1	9.5	0.4	96	8.85	9.05	0.2	98
"	"	9.05	9.45	0.4	96	8.8	.....	....	..
"	"	10.3	10.5	0.2	98	10.2	10.45	0.25	98
"	"	10.35	.....	....	..	10.15	.....	....	..
"	"	11.0	11 3	0.3	97	10.65	10.9	0.25	98
"	"	10.85	.....	....	..	10.6	.....	....	..
"	Hot pressed unstemmed.....	11.7	13.75	2.0	85	9.65	10.0	0.35	97
"	" "	11.8	.....	....	..	9.55	10.0	0.45	96
"	Hot pressed stemmed	11.45	12.25	1.3	90	9.3	9.6	0.3	97
"	" "	11.60	.....	....	..	9.25	9.5	0.25	97
"	" "	13.65	15.35	1.7	89	10.95	11.3	0.35	97
"	" "	.....	.....	...	..	10.8	11.2	0.4	96
Catawba	Cold pressed	12.35	12.6	0.25	98	11.85	12.2	0.35	97
"	"	12.35	.....	....	..	11.8	.....	....	..

[1] Fifty cc. samples were diluted to 250 cc. and digested in the cold with carbon black for about one hour except in case of the hot pressed juices which required repeated treatment with carbon black. Aliquots of 50 cc. were filtered off and titrated.

Each solution was prepared for titrations as follows: About 100 cc. of distilled water in a 150 cc. beaker were heated to boiling and 10 cc. or more of the sample added from a pipette. The beaker was covered with a watch-glass, the mixture brought just to boiling and then removed. The titration was made at once, using tenth-normal soda which contained a small proportion of barium hydroxide.

The results show that litmus readily titrates 96 to 99 per cent. of the organic acids in dilute solution in water, the amount shown by phenolphthalein being taken as 100 per cent.[1] In case of all of the juices except the hot-pressed Concord,

[1] In case of citric acid slightly more acid was indicated by litmus than by phenolphthalein, but this was possibly due to some impurity in the acid.

together, from 96 to 97 per cent. being now shown by litmus. This fact demonstrates a most serious objection to phenolphthalein—that the tannin and coloring matters are at least partly titrated when it is used, thus causing these substances to be partly or wholly estimated as constituents of the total acid, when unquestionably they should not be so included. This objection to the indicator is sustained by the observation of Hortvet[1] that whereas but 14.3 per cent. of gallotannic acid was titrated using litmus, 78.8 per cent. was estimated using phenolphthalein. Results on highly colored grape and other juices, and on many red wines, will probably be much too high if the latter indicator is used.

[1] *Loc. cit.*

SUMMARY.

(1) A slight change in the method of determining total tartrates, consisting in employing a 4-inch Büchner funnel instead of a Gooch crucible for collecting the crop of crystals, was found necessary when dealing with hot pressed Concord grape juice.

(2) The Scuppernong grape juices were considerably less rich than the other varieties in all constituents except total acid, and two out of the three varieties analyzed contained sucrose.

(3) The maceration of the cold-pressed Concord juice for sixteen hours had little effect on its composition.

(4) The hot-pressed Concord juices were considerably richer in solids than the cold-pressed, and this difference was due to slight increase in ash, total acids and total tartrates, an increase in nitrogen and decided increases in undetermined solids, and tannin and coloring matter.

(5) The Catawba grape juice was similar in composition to the cold-pressed Concord, but higher in total acids, total tartrates and protein.

(6) A method of using litmus due to C. S. Ash was found very useful. This method consists in employing a litmus which has been thoroughly exhausted with hot alcohol, and using a dilute neutral solution placed in small drops on a white glass surface as an outside indicator.

(7) With red grape juices using phenolphthalein it is shown that it is necessary to run a blank side by side with the sample being titrated in order to detect the change in shade due to the indicator.

(8) When dilute solutions of the commonly occurring organic acids were titrated, litmus was found to indicate from 96 to 99 per cent. of the acids, the amounts shown by phenolphthalein being taken as 100 per cent.

(9) When grape juice low in tannin and coloring matter was titrated, litmus indicated from 96 to 98 per cent. of the acids present.

(10) When juices high in tannin and coloring matter were titrated, but from 85 to 90 per cent. of the acids apparently present were indicated by litmus. After removing the tannin and coloring matter litmus indicated from 96 to 97 per cent. of the amounts of acid shown by phenolphthalein.

(11) Litmus is to be preferred to phenolphthalein in the titration of total acid in products containing appreciable quantities of tannin and coloring matter since by its use these substances are not appreciably titrated.

AMERICAN MOLASSES FEEDS: THEIR MANUFACTURE AND COMPOSITION.

By J. E. Halligan.

Received February 25, 1909.

The manufacture of molasses feeds in this country started about twelve years ago and since that time the demand for this class of feed has steadily increased until to-day it is one of the standard mixed feeds found on the American market. On account of the popularity for such a feed many mills are turning out molasses feeds exclusively.

The capacity of the mills vary from 50 to 500 tons per day, and they average about 100 to 150 tons a day.

There are several different methods employed in compounding these feeds for the trade, among which may be mentioned the following:

1. The molasses is mixed with the primary products (such as grain, chopped hay, etc.), without subjecting any of the materials to heat.

2. Cold molasses is added to the kiln-dried primary products and thoroughly mixed.

3. Hot molasses is mixed with cold primary products.

4. Hot molasses is mixed with artificially dried primary products.

Some manufacturers vary the above-mentioned methods by artificially drying their mixtures after the molasses has been thoroughly incorporated with the balance of the feed.

The temperature to which the molasses is heated varies in different factories but it is generally just warmed, although the best results are obtained when the molasses is brought to the boiling point.

Of the above methods, No. 4 has given fine results, both in lowering the moisture content and in preventing the feed from decomposing when put on the market. In the manufacture of wet feeds method No. 2 is often followed.

It is difficult to secure a good mechanical mixture when a small quantity of molasses is employed unless the molasses is heated before introducing it into the balance of the feed. The heating of the molasses before mixing allows of a more even distribution and drives off some of the water present in the molasses. Those feeds manufactured by using small amounts of cold molasses are liable to be lumpy and especially is this true when finely ground products such as cottonseed meal, rice polish, etc., are contained in the feed.

Most factories use a mixture of beet and cane molasses. There are some concerns that employ

either beet molasses or cane molasses entirely. When a mixture of beet and cane molasses is used the beet molasses generally predominates as the cane molasses is used to render the feed more palatable and to give it a pleasant aroma. In such cases when a mixture of beet and cane molasses is customary the cane molasses is often diluted with about 15 per cent. of water. The cane molasses is warmed and the molasses and water thoroughly mixed. The manufacturers claim they dilute the cane molasses to insure a more even distribution, but in all probability the water is added to reduce the cost of the feed as such feeds are not usually dried after the molasses is added. Beet molasses is never, or hardly ever, diluted with water as it is already fairly thin when delivered.

There are many combinations of materials introduced in these feeds, governed principally by the intelligence and honesty of the manufacturers. The location, demand, ease of obtaining and price of the feeding materials that go to make up the finished product are also important considerations in the selection.

Cottonseed meal, malt sprouts, dried brewers' grains, distillery products, rice bran, rice polish, rice hulls, corn, corn chops, corn bran, ground corn-cobs, ground corn-stalks, corn pith, wheat products (generally wheat screenings), dried beet pulp, oats (generally off-grade oats), oat hulls, finely ground or chopped hay (usually leguminous hays, such as alfalfa), straw, flax brands (including all weeds, dust, dirt and screenings from the flax seed as well as part of the shell and fiber of the flax), elevator dust (including grain smut, all sorts of brushings and cleanings, such as dust, grain rust, etc.), sweepings, grain screenings, refuse from flouring mills, cockle seeds and bran, ground peanut shells, weed-seeds (ground and unground), chaff from pipe factories and similar products are used in these feeds.

Some manufacturers use high protein concentrates such as cottonseed meal, dried brewers' grains, distillers' grains, etc., to fortify their feeds and they add inferior materials such as rice hulls, weed seeds, ground corn-stalks, elevator dust, grain screenings, ground straw, oat hulls, unsound grains of corn, etc., as a filler. The whole mixture is then concealed by the addition of molasses. It is possible for a manufacturer to put out such a feed as mentioned above and have it run as high in chemical composition as a feed made up of entirely high-grade products. There are many molasses feeds on our market composed of good clean standard products, but the molasses offers an excellent chance for the use of inferior materials by the unscrupulous manufacturer.

There are some people who do not sell a feed made up of the same feeding products all the time, but they change their mixtures two or three times a year, as they are sometimes unable to obtain the primary products at a price enabling them to sell at a profit. Others substitute materials to improve their feed or to increase their profits. Some high-class feeds have been offered to the trade and after a demand has been created low-grade materials have been substituted for the pure products that originally made up the feed.

There are two general classes of molasses feeds sold to our feeders, namely, horse feeds and dairy feeds. Poultry and calf feeds are also manufactured but these are exceptional. Most of the manufacturers prefer to handle the horse feeds because of the greater profits.

The quantity of molasses employed in these feeds varies from 10–60 per cent. Those feeds carrying 25 per cent. or more of molasses are usually classed as wet feeds (provided they are not artificially dried), and those containing less than 25 per cent. of molasses are termed dry feeds. There are many feeds that contain more than 25 per cent. of molasses which are subjected to a drying process and these are classed as dry feeds.

Wet molasses feeds are generally sticky and of darker color than other molasses feeds, due to the large amount of molasses present. In the North, some of the wet feeds form a hard cake in the cold weather and in such cases it is necessary to thaw them out before feeding. Below are a few analyses of wet molasses feeds:

WET MOLASSES FEEDS.

	I.	II.	III.	IV.	V.
Protein	11.69	12.88	15.95	6.52	15.60
Ether extract	0.54	0.74	2.75	1.79	3.82
Carbohydrates	43.33	36.94	49.45	51.92	45.32
Fiber	19.23	21.16	10.86	14.97	12.01
Water	16.41	18.47	16.10	14.20	16.65
Ash	8.80	9.81	4.89	10.60	6.60

I. and II. Chopped alfalfa and about 50 per cent. beet molasses.

III. Malt sprouts, brewers' grains, cottonseed meal and 30–40 per cent. cane molasses.

IV. Off-grade corn, cut straw, light oats, oat hulls and about 30–40 per cent. cane molasses.

V. Brewers' grains, malt sprouts, rice hulls, light oats, oat hulls, grain screenings, about 30–

40 per cent. beet molasses, and 10–20 per cent. cane molasses.

DRY DAIRY FEEDS.

Those molasses feeds sold as dairy feeds usually run high in protein and they are often fortified with some protein concentrate. The following analyses show the composition of the principal dry dairy feeds found on the American market.

	I	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Protein.........	13.90	17.80	16.22	14.35	17.00	17.13	18.94	18.31	14.26	16.14	16.10
Ether extract....	3.10	3.32	4.73	3.00	4.49	5.09	3.27	6.63	3.14	5.12	3.96
Carbohydrates .	52.44	52.03	51.17	48.96	50.17	46.87	50.86	49.38	53.93	43.41	48.77
Fiber	16.46	8.76	11.36	15.06	11.15	11.86	10.17	8.30	9.82	20.30	11.18
Water..........	7.20	10.23	9.20	10.68	11.30	11.97	10.99	9.72	11.60	8.10	12.15
Ash............	6.90	7.86	7.32	7.95	5.89	7.08	5.77	7.66	7.25	6.93	7.84

I. Corn, brewers' grains, malt sprouts, cottonseed meal, rice hulls, weed seeds, about 25 per cent. beet molasses and 5–10 per cent. cane molasses.

II. Off-grade corn, light oats, oat hulls, wheat screenings, malt sprouts, cottonseed meal, barley beards and screenings, about 25 per cent. beet molasses and 5–10 per cent. cane molasses.

III. Corn, off-grade oats, oat hulls, malt sprouts, brewers' grains, cottonseed meal, barley residues, rice hulls, weed seeds, about 20–30 per cent. beet molasses and 5–10 per cent. cane molasses.

IV. Corn, dried brewers' grains, malt sprouts, elevator dust, wheat and buckwheat screenings, about 25–30 per cent. beet molasses and 5–10 per cent. cane molasses.

V. Cottonseed meal, wheat screenings, light oats, oat hulls, off-grade corn, weed seeds, about 20–25 per cent. beet molasses and 5–10 per cent. cane molasses.

VI. Corn, ground corn-stalks, ground corn-cobs, off-grade oats, barley, cottonseed meal, distillery products, elevator dust, weed seeds, about 25 per cent. beet molasses and 5 per cent. cane molasses.

VII. Brewers' grains, malt sprouts, cottonseed meal and 25–30 per cent. cane molasses.

VIII. Corn, rice bran, rice polish, cottonseed meal and 15–30 per cent. cane molasses.

IX. Corn bran, oat hulls, light oats, off-grade corn, elevator dust, wheat and buckwheat screenings, malt sprouts, distillery residue, about 25 per cent. beet molasses and 5–10 per cent. cane molasses.

X. Flax brands (including all weeds, dust, screenings and dirt from the flax seed as well as part of the shell and fiber of the flax), elevator dust, light oats and hulls, cottonseed meal, about 25 per cent. beet molasses and 5–10 per cent. cane molasses.

XI. Corn products, distillers' products, cottonseed meal, elevator dust and about 35 per cent. beet molasses.

DRY HORSE AND MULE FEEDS.

Those feeds sold for horse and mule feeds carry more carbohydrates and less protein than the dairy feeds, as the accompanying analyses show:

I. Distillery products, ground corn-stalks, ground corn-cobs, light oats, oat hulls, cottonseed meal, weed seeds, about 25 per cent. beet molasses and 5 per cent. cane molasses.

II. Corn chops, rice bran, rice polish, cottonseed meal, and 15–30 per cent. cane molasses.

III. Corn chops, wheat bran, cottonseed meal, alfalfa, and 15–25 per cent. cane molasses.

IV. Corn chops, cottonseed meal, Lespedeza hay (chopped), and 20 per cent. cane molasses.

V. Dried brewers' grains, chopped alfalfa, corn chops, cottonseed meal, elevator dust, and 25–30 per cent. cane molasses.

VI. Chopped alfalfa, corn, oats (off-grade), barley and about 25 per cent. beet molasses.

	I	II	III	IV.	V.	VI.	VII.	VIII.	IX	X.	XI.
Protein.........	11.68	11.98	11.56	11.06	12.69	10.78	8.84	12.48	11.13	12.00	13.70
Ether extract...	3.70	5.89	4.77	1.75	5.80	2.42	2.80	3.26	7.26	6.50	5.42
Carbohydrates .	56.67	51.79	59.18	49.73	55.23	61.95	53.91	53.01	54.96	51.52	40.43
Fiber..........	10.29	11.15	6.00	22.37	9.12	8.06	12.75	13.89	8.47	10.32	20.92
Water..........	11.97	11.05	11.83	9.18	9.72	12.00	12.69	11.26	11.62	11.31	12.85
Ash	5.69	8.14	6.66	5.91	7.44	4.79	9.01	6.10	6.56	8.35	6.68

VII. Corn, light oats and hulls, sweepings and 25 per cent. cane molasses.

VIII. Light oats, corn product, wheat screenings, cottonseed meal, linseed meal, weed seeds, about 15–20 per cent. beet molasses and 5–10 per cent. cane molasses.

IX. Corn chops, chopped alfalfa, rice bran, cottonseed meal and 15–25 per cent. cane molasses.

X. Dried brewers' grains, chopped alfalfa, rice bran, elevator dust, corn chops (off-grade), cottonseed meal and 15–30 per cent. cane molasses.

XI. Distillers' grains, cottonseed meal, flax brands, weed seeds, elevator dust, about 25 per

cent. beet molasses, and 5–10 per cent. cane molasses.

FOREIGN MOLASSES FEEDS.

The analyses of a few German molasses feeds and the Toury peat-molasses combination is given for comparison:

ANALYSES OF GERMAN MOLASSES FEEDS.

	I*a*.	II*a*.	III*a*.	IV*b*.	V*b*.	VI*b*.	VII*a*.	VIII*c*.
Protein	12.71	14.65	11.31	24.62	25.00	29.55	15.25	8.90
Ether extract	1.88	4.44	4.67	1.04	0.14	0.22	2.19	0.35
Carbohydrates	48 02	53.58	56.40	53.02	50.98	50.89	49.90	59.45
Fiber	12.00	3.41	5.52	7 02	9.77	6.24	3 07	14.40
Water	18.33	17.69	16.50	7.33	8.51	8.53	20.85	9.00
Ash	7.06	6.23	5.60	6 97	5.60	4.57	8 74	7.90

I. Palm oil meal and molasses—average of two analyses.

II. Corn germ and molasses—average of three analyses.

III. Wheat bran and molasses.

IV. Wheat bran, blood and molasses.

V. Brewers' grains, blood, bran and molasses.

VI. Dried cossettes, blood and molasses.

VII. Cocoanut cake and molasses.

VIII. Dried cossettes and molasses.

In all probability the above feeds contain beet molasses entirely.

a. Ware—Cattle Feeding—page 294.

b. Ware—Cattle Feeding—page 283.

c. Ware—Cattle Feeding—page 260.

THE TOURY PEAT-MOLASSES COMBINATION (*d*).

Water 19.00 per cent., ash 8.91 per cent, sugar 31.70 per cent, soluble substances 20.93 per cent, insoluble substances 19.46 per cent. This molasses fodder consists mainly of 24 per cent. peat and 76 per cent. slightly steamed diluted molasses.

d. Ware—Cattle Feeding—page 265.

AMERICAN MOLASSES FEEDS.

One per cent. or less of salt is put into some of these feeds to make them more palatable.

On account of the acidity of Louisiana molasses, due to the use of sulphur in the manufacture of sugar from the cane, feed manufacturers sometimes neutralize this acidity by adding lime-water or sodium hydrate. It has been found impracticable to use lime-water as the lime separates out and shows in the feed.

There has been considerable trouble experienced with molasses feeds on account of fermentation setting in and spoiling the feed. Some manufacturers have eliminated this trouble almost completely by proper and careful manufacture. Fermentation is caused by using unsound primary products, such as previously fermented corn, etc., and by improper drying of the feed. Oftentimes cane molasses ferments on the plantations before being purchased and when such fermented molasses is put into a feed without proper treatment, the usual result is the deterioration of the feed. The simple warming of fermented molasses is not sufficient but it must be brought to a boil to arrest the fermentation completely. When a mixture of beet and cane molasses is employed and the diluting of the cane molasses with water is practiced, the result is generally a spoiled feed, due to fermentation.

One manufacturer told me that he had to discontinue the use of beet molasses in his wet feed as fermentation invariably set in and decomposed the feed. As a whole, it is a safe policy to boil the molasses, be it cane or beet, as such procedure tends to arrest fermentation and it also results in driving off a great deal of water, which keeps down the moisture content.

A one-hundred pound sack of feed, composed of a mixture of dried brewers' grains, malt sprouts, cottonseed meal and 35 per cent. cane molasses, was left on a wharf, which had a roof but was open on all sides, for two months, on the banks of the Mississippi River at Baton Rouge, Louisiana. At the end of that time this feed was in perfectly sound condition. There was some loss of moisture but otherwise no change took place in the feed. The test was fair for there were three heavy rains during the period and considerable damp weather. According to a test run by a large manufacturer of molasses feeds, cane molasses seems to have better keeping qualities than beet molasses. This test took place in the middle west in the summer. The beet molasses was kept in a tank and drawn on from time to time without complete emptying, and the tank was filled at frequent intervals. In the course of one month fermentation set in. The same test was tried with cane molasses under the same conditions and it took three and a half months for fermentation to start, necessitating the thorough cleansing of the tank. This manufacturer says: "often the tank containing the cane molasses does not ferment until the end of four months but the

beet molasses will not keep more than a month under our conditions."

The use of beet or cane molasses, or a mixture of both in varying proportions, in molasses feeds, is a problem yet to be determined by many manufacturers. Keeping qualities, palatability, effect on the animals and popularity of the feed are some of the problems to be considered.

Just about twelve years ago Louisiana blackstrap was a nuisance and the sugar planters had a hard time to dispose of it. On account of its value for feeding purposes the demand has become so great that it is now selling for $19 to $21 per ton retail, perhaps the highest figure it has ever reached. Louisiana blackstrap has been so scarce that some of our feeders are purchasing second molasses for feeding purposes. The time is coming when our manufacturers of commercial molasses feeds will be forced to obtain some of their supply of cane molasses from the tropical countries.

On the whole, there is a bright future for molasses feeds even at the high prices feeds are carrying. It is possible for manufacturers to put out wholesome feeds free from adulteration with inferior products and make a good profit. In the past two years there has been a great improvement in this class of feed, and some concerns have been forced to go out of business on account of flagrant adulteration of their feeds. The time has come when only those feeds that are pure and honest mixtures will meet with success, as adulterated feeds even if they do have a high chemical composition, most always show poor results on the animals to which they are fed.

LOUISIANA STATE EXPERIMENT STATION,
BATON ROUGE, LA.

A RAPID METHOD OF HYDROLYZING STARCH.

By GEO. A. OLSON.

Received May 3, 1909.

Numerous methods for the hydrolyzing of starch have been devised in the past, among which may be mentioned Sachsse's,[1] Märker's,[2] Guichard's,[3] and others. Chemists who have tried these methods know what a long and tedious procedure it is to wash and hydrolyze materials according to any one of them. After a futile attempt to find a method that would give concordant results, the members of the A. O. A. C. finally adopted the Sachsse method as official.[1] While this method gives fairly satisfactory results, it still has the disadvantage of time when compared with the method which will be discussed in the following pages. Where two and one-half hours were required to hydrolyze starch it is now possible to accomplish this in about four minutes.

Preparation of Samples.—Before discussing this method, it is deemed advisable to give a few suggestions as to the preparation of the samples to be hydrolyzed. Too much stress cannot be laid upon the importance of securing a uniform, representative sample. The material should be finely ground and thoroughly mixed. In case of some substances, *e. g.*, oats, etc., it is preferable after the first grinding to separate the hulls from the starchy material and grind separately, thus insuring a more uniform mixture.

Method of Hydrolysis.—Place in a 500 cc. Kjeldahl flask one gram of material. Tap the neck of the flask in order to settle the fine particles adhering to the sides. Mix with this weight ten cc. of distilled water and rotate slowly and steadily (one revolution per second) so as not to wash any of the sample too high up on the sides of the flask. Next cautiously add 6 cc. of sulfuric acid (specific gravity 1.84) and rotate somewhat more rapidly than in the first instance. After the acid and material have been thoroughly mixed hold the flask in one hand over a flame about two inches high and rotate about one revolution per second at first and then as the mixture increases in temperature rotate with an accelerated motion up to five revolutions per second. Continue rotating at this rate until the mixture becomes nearly transparent. At this stage add 10 to 15 cc. of distilled water, continue rotating and heat again, this time to boiling, cool, neutralize with sodium hydroxide (using phenolphthalein as indicator), cool again, transfer to 250 cc. volumetric flask, fill with distilled water to mark and proceed according to one of the recognized methods for dextrose determination.

Notes on Manipulation.—The hydrolysis commences with the addition of acid. In case of cereals, bran, shorts, etc., a slight coloring is first observed, then a milkiness, and finally the solution becomes almost transparent, varying in color from straw to a light brown. A further heating intensifies the color, and if this process is continued too far there is danger of caramelizing a part of the

[1] *Chem. Centralbl.*, 1877, p. 732; *Journ. Anal. Chem.*, II, 153.
[2] *Chem. Zeit.*, IX, 319; *Ztschr. anal. Chem.*, **24**, 617.
[3] *Bull. d. l. Soc. Chim. d. Paris* [3], **7**, 554.

[1] *U. S. Dept. of Agr., Bur. of Chem., Bull.* **107** (rev. ed.), p. 53.

dextrose formed. Since no sharp line can be fixed, it will be necessary for the operator to use some judgment as to the extent that this process should be continued. A moderate overheating does not materially affect the results. On the second addition of water a milkiness reappears which again disappears on heating. In most cases there is enough coloring matter present in the material to act as an indicator; phenolphthalein, however, gives a sharper color and is therefore recommended. If the material tends to creep up on the sides of the flask during the rotating process, a slight agitation will obviate the difficulty. The time required to hydrolyze eight samples, comprising oats, barley, wheat and corn, was thirty minutes or a little less than four minutes for each sample.

Hydrolysis of Substances that Do Not Mix Well.—Occasionally it happens that the substance to be analyzed is difficult to mix uniformly. Under such circumstances larger samples should be used for the hydrolysis; from 2 to 5 grams of material can be as readily hydrolyzed as 1 gram. When larger quantities of material are taken the proportion of water and acid must be increased correspondingly, *e. g.*, with 5 grams of material add 50 cc. of water and 30 cc. of acid. With larger amounts of material, however, it is more difficult to determine the stage when the starch is completely hydrolyzed.

Accuracy of Method.—A considerable number of comparative analyses have been made by the official method (Sachsse) and the one herein described. The figures given in the following table and taken at random show the substantial accuracy of the method. The preliminary washing required by the official method is not followed in the one devised by the writer. A separate determination for sugar will be necessary for materials containing appreciable amounts of this component. Allihn's[1] method for sugar was used and the copper weighed as cuprous oxide.

It will be noted from the results given in the following table that slightly higher values for starch were obtained with the new method, probably due to the fact that the samples were not treated with alcohol, ether and water previous to hydrolysis. By omitting the preliminary washing much time was saved, particularly with legumes and oil meal; in some cases from five to eight hours were required to wash the samples before they were ready for hydrolysis.

[1] *U. S. Dept. of Agr., Bur. of Chem., Bull.* **107** (rev. ed.), p. 49.

COMPARATIVE RESULTS WITH NEW AND OFFICIAL METHOD.

	Official method. Starch, per cent.	New method. Starch, per cent.
Peas	44.03	44.73
	44.31	44.27
Oats	41.67	42.03
	42.13	42.48
Oats	41.54	41.83
	41.80	42.03
Wheat	52.92	52.74
	52.61	52.84
Wheat	45.90	46.33
	46.09	46.01
Wheat	53.48	53.84
	52.91	53.42
Barley	54.45	54.63
	54.21	54.16
Barley	54.87	55.62
	55.31	55.53
Potatoes (dry)	66.78	66.78
" (calc. in original)	16.34	16.34
Potatoes (dry)	69.03	69.53
" (calc. in original)	17.48	17.60
Oil meal	21.60	21.69
White corn	59.40	59.69
Yellow corn	56.61	56.34
Soy beans	9.93	10.50
Soy bean cake	8.17	8.63
Bran	44.57	45.80
Shorts	51.85	53.18
Baking powder	25.34	26.64
Baking powder	37.80	37.89

Diastase Method.—With one single exception (malt) the diastase method gave lower starch values than either of the other two, *e. g.*, white corn 55.44 per cent., potatoes (first one in table) 62.93 per cent., and bran 38.63 per cent. The material was gelatinized by boiling with water containing 1 per cent. of glycerol, cooled and converted with Merck's pure diastase.[1] The blue color with iodine was in evidence for hours. Disregarding the preliminary washing, a sample of malt gave 59.31 per cent. starch by Sachsse method, 59.40 per cent. starch by the writer's method and 59.40 per cent. starch by mashing. The mashing was conducted at temperatures increasing from 45 to 73° C. for one-half hour and maintained at 73° C. for another half hour.

Value of Starch Determination in Feeding Stuffs.—The starch content of a cereal, potato, or a feeding stuff is as valuable a component as a fat, protein or ash constituent, yet it is seldom determined. It has been the custom in the past, especially in fodder analyses, to call the undetermined constituents *nitrogen-free extract* or *carbohydrates*, and in turn the carbohydrates are frequently spoken of as *starch*. With the new method it is now possible to determine with facility the acid-hydrolyzable part of nitrogen-free extract and thus reduce the undetermined constituents to a minimum.

[1] Bought at least three years ago.

When a starch is hydrolyzed with an acid, there is, of course, always the danger of converting a part or all of the pentosans, cellulose and allied bodies into sugars. Again the rôle played by diastase upon starch has not been settled. If, however, the analyst is content in reporting 6.25 times nitrogen as protein, the ether extract as fat, and the residue obtained after boiling the ether-extracted material with acid and alkali as crude fiber, then on equally good grounds he should be content in reporting starch as obtained by acid hydrolysis.

CHEMICAL LABORATORIES,
WASHINGTON STATE EXPERIMENT STATION,
PULLMAN, WASHINGTON.

THE PREPARATION OF SOIL SAMPLES FOR CHEMICAL ANALYSIS.

By G. M. MACNIDER.

Received March 15, 1909.

The following investigation was undertaken to determine the proper sized sieve to use in preparing soil samples for chemical analysis when the total amount of plant food elements are to be determined. When the available or soluble plant food is determined, by the Official Method of the Association of Official Agricultural Chemists or by some other method using some solvent to abstract the plant food, a preparation using a sieve with perforations smaller than 2 mm. in diameter seems to be adequate, as it has been shown by several investigators that the greater portion of the soluble plant food is found in the smaller particles of the soil, *i.e.*, the very fine sands, silt and clay. The Official Method of preparation has, however, been recently changed from 0.5 mm. sieve to 1 mm. sieve.[1]

The size of sieve to be used, which is to determine what portion of the soil shall be taken for analysis, is of course an arbitrary standard. In making total analyses it is very necessary that the standard adopted be such that the analyses will give the fairest idea of the plant food contained in the soil. With some very coarse soils even the 2 mm. preparation excludes from the analysis particles which it would seem should be included. From the data here presented and from a large number of chemical analyses of soils made in this laboratory we have arrived at the conclusion that the most satisfactory method of preparation, when the total plant food constituents are to be determined, is to pass the sample through a sieve having circular perforations 2 mm. in diameter and take the portion passing the sieve as the "fine earth" which is to be analyzed and to regard the portion not passing the sieve as coarse gravel which should not be classed as "fine earth" or soil. This method also gives a uniform preparation for both the chemical and mechanical analyses.[1]

The method of preparation is as follows: Spread the sample on a board covered with heavy paper and roll with a wooden rolling pin to break up lumps. The sample is then passed through a sieve having circular perforations 2 mm. in diameter. If there are any coarse particles they should be put in a mortar and rubbed with a rubber-tipped pestle to remove the adhering, fine particles. This operation should be repeated till the coarse particles are clean. When all the fine particles have been passed through the sieve the sample should be thoroughly mixed before the portion for analysis is taken out. In some samples the large particles passing the 2 mm. sieve may be large enough to interfere with the fusion in the analysis. In such cases a portion may be pulverized for the determinations requiring fusion.

In the following table are analyses of representative soils made on the 0.5 mm. preparation and on the 2 mm. preparation. The 0.5 mm. was taken for comparison as this was for a number of years the official method of preparation of soil samples and a large number of analyses have been made in this laboratory on that preparation. The table shows the percentages of plant food constituents and the pounds per acre of each constituent to a depth of 8 inches, calculated from the apparent specific gravity, also the apparent specific gravity and the per cent. of fine soil passing the sieve in each preparation. The samples have been selected so as to represent a large variety of soils in North Carolina, the sands and sandy loam soils of the Atlantic Coastal Plain, the coarse sandy loams of the Piedmont Plateau and the sandy loams of the Mountain Region. Comparative analyses were not made of the clay and loam soils as practically all of these pass the 0.5 mm. sieve.

DISCUSSION OF RESULTS.

Reference to the table will show the differences in the analyses so that it is only necessary here to point out a few of the more marked differences.

[1] *U. S. Dept. of Agr., Bur. of Chem., Bull.* **107** (revised).

[1] The method of mechanical analysis in use in this laboratory is the same as that used by the Bur. of Soils. See *Bull.* **24**, *Bur. of Soils*, by L. J. Briggs.

COMPARISON OF ANALYSES OF SOILS PREPARED BY PASSING SAMPLES THROUGH 0.5 MM. SIEVE AND THROUGH 2 MM. SIEVE.

		Analyses of samples prepared through 5 mm. sieve.											Analyses of samples prepared through 2 mm sieve.										
Laboratory number.	Soil type.	Per cent. fine soil.	Apparent specific gravity.	Volatile matter. Per cent.	Nitrogen. Per cent.	Nitrogen. Pounds per acre.	P_2O_5. Per cent.	P_2O_5. Pounds per acre.	K_2O. Per cent.	K_2O. Pounds per acre.	CaO. Per cent.	CaO. Pounds per acre.	Per cent. fine soil	Apparent specific gravity.	Volatile matter. Per cent.	Nitrogen. Per cent.	Nitrogen. Pounds per acre.	P_2O_5. Per cent.	P_2O_5. Pounds per acre.	K_2O. Per cent.	K_2O. Pounds per acre.	CaO. Per cent.	CaO. Pounds per acre.
287	Tobacco soil—soil	45.9	1.47	1.71	0.08	2129	0.07	1863	4.17	110999	0.37	9848	92.1	1.73	1.12	0.03	939	0.06	1879	2.14	67039	0.07	2192
288	Tobacco soil—subsoil	49.1	1.34	1.17	0.13	2754	0.05	1059	4.26	90253	0.38	8050	90.6	1.68	0.74	0.01	304	0.06	1225	2.34	65185	0.07	2129
289	Tobacco soil—soil	55.8	1.32	1.75	0.11	2629	0.05	1195	4.29	102541	0.53	12668	93.2	1.49	1.30	0.02	539	0.05	1349	2.43	65563	0.09	2428
290	Tobacco soil—subsoil	63.8	1.15	3.42	0.17	3540	0.04	832	3.91	81422	0.49	10203	95.1	1.27	1.50	0.02	462	0.05	1154	2.84	55595	0.11	2540
639	Porter's sandy loam—soil	73.5	1.11	8.22	0.09	1809	0.08	1608	4.26	85615	0.30	6029	87.3	1.22	6.30	0.08	1767	0.10	2209	4.00	88366	0.31	6848
640	Porter's sandy loam—subsoil	92.0	0.99	10.19	0.03	537	0.12	1951	3.67	65791	0.05	896	100.0	1.10	9.41	0.02	398	0.09	1792	1.70	33861	0.11	2191
648	Porter's sandy loam—soil	94.6	1.36	4.06	0.04	975	0.05	1231	4.22	102925	0.12	2955	100.0	1.37	3.52	0.03	744	0.05	1240	4.26	105761	0.22	5457
649	Porter's sandy loam—subsoil	93.7	1.22	7.89	0.03	662	0.06	1325	3.09	68263	0.05	1104	100.0	1.27	7.57	0.03	692	0.06	1386	3.12	72062	0.11	2540
750	Norfolk sandy loam—soil	82.7	1.41	2.16	0.07	1787	0.02	510	1.71	43659	0.22	5617	100.0	1.47	1.89	0.03	798	0.08	2129	1.42	37798	0.21	5589
751	Norfolk sandy loam—subsoil	83.8	1.37	2.70	0.03	744	0.11	2728	1.62	30188	0.18	4465	100.0	1.41	2.62	0.02	510	0.13	3319	1.67	42638	0.22	5617
772	Portsmouth sandy loam—soil	88.5	0.98	19.00	0.42	7453	0.05	887	1.13	20052	0.06	1064	100.0	1.04	19.56	0.51	9604	0.07	1318	1.03	19397	0.10	1883
773	Portsmouth sandy loam—subsoil	84.3	1.22	6.07	0.11	2430	0.02	441	1.46	32253	0.12	2650	100.0	1.30	4.97	0.08	1883	0.04	941	1.25	29425	0.09	2118
839	Norfolk sand—soil	59.6	1.45	3.04	0.03	787	0.03	787	0.12	3150	0.20	5251	99.8	1.45	2.12	0.03	787	0.08	2100	0.04	1050	0.14	3675
840	Norfolk sand—subsoil	61.8	1.41	2.08	0.03	765	0.04	1021	0.15	3829	0.20	5106	99.8	1.42	1.51	0.03	771	0.06	1542	0.10	2571	0.24	5171
841	Norfolk sandy loam—soil	81.7	1.47	2.29	0.03	798	0.01	266	0.12	3194	0.18	4791	100.0	1.53	1.96	0.03	831	0.02	554	0.08	2216	0.19	5264
842	Norfolk sandy loam—subsoil	82.9	1.28	3.65	0.02	463	0.02	370	0.25	5794	0.24	5562	100.0	1.34	3.87	0.02	485	0.04	970	0.16	3882	0.14	3397
843	Norfolk sandy loam—soil	75.7	1.44	2.34	0.04	1043	0.02	417	0.21	5474	0.19	4954	100.0	1.51	2.09	0.03	820	0.03	820	0.11	3007	0.09	2460
844	Norfolk sandy loam—subsoil	75.7	1.41	1.32	0.02	510	0.01	255	0.30	7659	0.25	6383	97.0	1.45	1.06	0.02	525	0.02	525	0.23	6038	0.14	3675

All analyses calculated to dry basis.

The analyses in this table were made in this laboratory by the author and Messrs. Haywood, Pickel, Perkins and Brinkley.

The most marked differences to be noted are in the percentages of soil passing the different sieves and in the percentages of potash and lime. There are also differences in the percentages on nitrogen and phosphoric acid, but as the nitrogen is derived from organic sources and the phosphoric acid also to a large extent, the differences are not so marked.

The coarse particles from all the samples were examined microscopically to determine what minerals were present, so that this could be taken into consideration in interpreting the analyses.

Nos. 287 to 649 inclusive are residual soils from the Piedmont and mountain regions, derived from granitic rocks.

In No. 287 only 45.9 per cent. of the sample passed the 0.5 mm. sieve, while 92.1 per cent. passed the 2 mm. sieve. The per cent. of potash is 4.17 on the 0.5 mm. and only 2.14 on the 2 mm. The difference in the per cents. of lime are also marked on this sample, being 0.37 on the 0.5 mm. and 0.07 on the 2 mm. The microscopic examination of the coarse particles from this sample showed them to be mostly quartz with some orthoclase. The chemical analysis of the coarse particles between 0.5 and 2 mm. showed 0.3 per cent. potash. The subsoil of this sample No. 288 shows about the same differences.

With Nos. 289 and 290 a slightly larger amount of soil passed both the 0.5 and 2 mm. sieves. The differences in the percentages are equally as marked as in the preceding samples.

In No. 639 73.5 per cent. soil passed the 0.5 mm. sieve and 87.3 per cent. passed the 2 mm. sieve, the difference being much less marked than in the preceding samples. The difference in the percentages of potash and lime are very slight, 4.26 per cent. potash on the 0.5 mm. and 4.00 per cent. on the 2 mm.; 0.30 per cent, lime on the 0.5 mm. and 0.31 per cent. on the 2 mm. The microscopic examination of the coarse particles showed them to be quartz with considerable amount of feldspar, which accounts for the percentages of potash and lime remaining practically the same on both preparations. This is in marked distinction to the preceding samples where the coarse particles were made up almost entirely of quartz and the differences in the percentages of potash and lime on the two preparations very marked. With the subsoil of this sample No. 640 the coarse particles contained considerably less potash feldspar,

hence the difference in the per cent. of potash on the two preparations.

Nos. 648 and 649 show quite similar results to No. 639 both in the percentages of fine soil passing the sieves and in the percentages of potash.

Nos. 750 to 844 inclusive are representative samples of the coarser soils of the Atlantic Coastal Plain. The differences in the percentages of soil passing the two sieves are very similar, all or practically all of the sample passing the 2 mm. sieve and only from 59.6 to 88.5 per cent. passing the 0.5 mm. sieve. The difference in the percentages of potash are also very similar, *i. e.*, the per cent. being considerably lowered when more of the sample is analyzed on the 2 mm. preparation than on the 0.5 mm. The microscopic examination of the coarse particles from these samples showed them to be composed almost entirely of pure quartz.

From the table and microscopic examinations it will be seen that the greater portion of the plant food is found in the soil particles less than 0.5 mm. in diameter, that is, the particles between 0.5 and 2 mm. in diameter are composed chiefly of quartz, the exceptions to this being the samples in which there was only a slight difference in the analysis on the two preparations and the microscopic examination of the coarse particles showed them to contain considerable amounts of feldspar.

If we assume that the particles of soil less than 2 mm. in diameter fairly represent what should be termed the soil from which the plant derives its food, it is evident that in making determinations of the total plant food, the analysis if made on a sample prepared through a sieve with perforations less than 2 mm. in diameter, *i. e.*, 0.5 mm., will show the soil to contain considerably more plant food than the soil from which the plant must derive its food and hence does not fairly represent the composition of the soil.

North Carolina Department of Agriculture,
Division of Chemistry.

THE CHANGES IN CRUDE PETROLEUM EFFECTED BY DIFFUSION THROUGH CLAY.

By David T. Day and J. Elliott Gilpin.

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That the process of diffusion through clay and shale and the replacement by water have been important factors in the concentration of petroleum in certain places was pointed out by Day in 1897[1] and is shown very clearly by recent work of Gilpin and Cram.[1] Suppose, for example, the petroleum formed in the deeper portions of the earth finds access through a seam or other opening to a layer of fine-grained clay or shale. It will diffuse through the material if the latter is finely divided, but would be stopped by material too coarse for capillary diffusion. These authors have found that the oil will rise in tubes packed with fuller's earth and in so doing is partly fractionated. By using several tubes and uniting oils of the same specific gravity, oil of different grades can be collected in sufficient quantity to be fractionated again, and the process can be continued until oils are obtained which are not altered by further passage through tubes filled with fuller's earth.

If such a diffusion took place in a large mass of clay no accumulation of oil would be found at any one spot, and a well drilled in this material would show only a small percentage, say 5–10 per cent., of petroleum. If now, as has been shown by Gilpin and Cram, water, either surface or subterranean, comes in contact with this clay it will diffuse into it and displace 2/3–3/4 and perhaps, in long geological periods, even more of the petroleum.

If the water surrounds the mass of clay the oil cannot escape and is driven finally into the coarse adjacent layers such as sandstone and gravel. The oil will remain in this position as it cannot be displaced by any capillary action of water on the rock.

The pressure under which it could accumulate would be entirely independent of hydrostatic pressure, and pressures equivalent to those observed in the phenomenon of osmosis can be brought about without an amount of water more than sufficient to saturate the clay itself—practically an infinitely smaller amount of water than is required for producing hydrostatic pressures equivalent to the pressures found in oil wells. These pressures are usually from 50 to 300 lbs. to the square inch—clearly within the range of osmotic pressure.

Pressures as high as 1500 lbs. per square inch have been claimed for natural gas, but it is not to be supposed that all accumulations of oil and natural gas are attributable to the phenomena here under consideration. The various conditions of accumulation of petroleum, however, are so easily explained by the driving out of oil by water,

[1] *Proc. Amer. Philos. Soc.*, Vol. XXXVI, No. 154.

[1] *Amer. Chem. Jr.*, **40**, 495.

that it seems extremely probable that many petroleum accumulations are due to this action. The process by which these facts have been established is as follows: tin tubes 5 feet and 1 1/4 inches in diameter, closed at the bottom with corks along whose sides, grooves were cut to admit the oil, were packed with fuller's earth, the earth being introduced in small quantities at a time and packed by a ramrod before the next lot was added. These were then placed in vessels containing petroleum and the air in the tubes was removed by a suction pump to facilitate the diffusion. After the oil had nearly reached the top of the tubes the clay was removed in sections and treated with water to displace the oil.

If a little water is added to the earth as removed from the tubes, after standing a few minutes all the water will pass into the earth and this will be accompanied by the liberation of oil. Oil so liberated can then be poured off directly from the earth without the labor of churning. When water first begins to liberate oil, the earth is granular; but when more water has been added and the last of the oil recovered, the earth has the consistency of a thin paste that will flow when the dish is inclined, which it will not do when the oil begins to come off.

All the oil from one section of a tube is of the same color irrespective of whether it is the first or the last oil to come off when water is added. It was assumed at first that all the oil which came from one section of earth had the same specific gravity, but this was found later not to be the case. The first oil to be collected, if taken in sufficiently small volume, say about 20 cc., is slightly heavier than the next portion. If as much as 100 cc. are included in the first sample, however, this will not be true. Beginning with the second sample the successive portions of oil steadily increase in specific gravity, the gradual addition of water affording another means of fractionation in addition to the separating power of the earth. Both of these methods of separation have been combined in this investigation. The earth must be thoroughly mixed after each addition of water to prevent a layer of water-wet earth from isolating earth that contains oil from the water added.

The petroleum used was a dark green oil from Venango County, Pa., of specific gravity 0.810. When 950 cc. of this oil were drawn upward in a tin tube 5½ feet long, the following separation was obtained:

TABLE I.—FRACTIONATION OF CRUDE PETROLEUM IN SINGLE TUBES.

	1.		2.		3.	
Time required, in hours	23.5		17.5		17.5	
Distance from top of tube to oil when opened, in centimeters	31		28		28	
	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic centimeters.
A, 8 centimeters at top.	0.796	42	0.8012	30	0.8022	18
B, next 8 centimeters..	0.808	45	0.804	37	0.803	35
C, next 18 centimeters.	0.8125	75	0.807	47	0.8075	66
	0.8137	24	0.809	22	0.810	25
D, next 30 centimeters	0.815	130	0.8125	148	0.812	140
E, next 35 centimeters..	0.818	170	0.8185	190	0.8175	145
F, rest	0.8205	125	0.823	100	0.821	105
		611		574		534

The oil in grade C was collected in two portions, the second being obtained by the addition of more water after the first lot of oil was poured off. Although 950 cc. of crude petroleum were used in each experiment, it will be noticed that the oil recovered measures much less than that. When several tubes were worked up together, in one test 9,070 cc. of crude petroleum yielded 5,951 cc. of oil and in another 8,915 cc. gave 5,415 cc.

That the addition of water in small portions acts as a fractionating agent in addition to the action of the clay is clear from a consideration of the following table:

When the first portion of oil was liberated, the mass was of the consistency of bran, but as more water was added it turned to a fluid paste. When water was added and the pail inclined, oil would continue to drain out for half an hour or longer before the addition of more water became necessary. The oil which was liberated by one lot of water, therefore, could be collected in several portions, and this was done to see whether the oil which comes off immediately after the addition of water is the same as that which drains out later. The letters I, II, etc., indicate that the fractions included were liberated by one addition of water.

TABLE II.—FRACTIONATION OF OIL OF GRADE E.

	Specific gravity	Cubic centimeters.		Specific gravity.	Cubic centimeters.
I..........	0.821	25	IV..........	0.8208	575
II	0.818	70		0.8222	55
	0.818	70	V..........	0.824	170
	0.8193	250		0.828	16
III..........	0.818	395	VI..........	0.827	95
	0.818	350		0.830	45
	0.818	460			
	0.820	60			

The first fraction is regularly of higher specific gravity than those immediately following if only enough water is added to liberate a first fraction of small volume, say about 20 cc. As the fraction

first obtained becomes larger in volume, it approaches nearer to the second fraction in specific gravity, and will even fall below that fraction if the volume is made too large.

The range of specific gravity covered by this first fractionation of the crude petroleum of specific gravity 0.810 was from 0.800 to 0.830. Fractions of the same specific gravity and of the same grade were united and the products chilled and filtered to remove all the dissolved paraffin possible. This was done out of doors toward the last of December, when the thermometer stood at about 4 to 8° C. Lower temperatures would not only throw paraffin out of solution, but cause the whole oil to thicken. The oils were filtered through large plaited filters of drying paper, twenty-four hours or more being required for many of the filters to empty completely. The lighter oils in Sections A and B deposited no paraffin. Some of the heavier grades deposited as much as 10 per cent. of their weight, accompanied in many cases by a slight change in specific gravity.

Oil of the same specific gravity was refractionated and the process continued up to the fourth generation. The oil obtained in this fractionation has the following specific gravities:

colorless. On evaporation of the ether there remained about 8 cc. of a heavy oil with the color of the natural petroleum. Pressure, heat, and extraction with ether together gave about half the amount of oil which the earth must have contained.

Earth that had been used once was allowed to dry for several weeks at room temperature until it had lost all appearance of containing moisture. It was then pulverized, sifted, and 720 grams used in a tube with 740 cc. of the crude petroleum of specific gravity 0.810, with the following results:

Table IV.—Fractionation of Crude Petroleum with Earth that Had Been Used Once.

	Specific gravity.	Cubic centimeters.
8 centimeters at top	....	0
Next 8 centimeters	0.8284	10
Next 18 centimeters	0.8225	45
Next 30 centimeters	0.8143	60
	0.8155	80
Rest	0.8175	83
	0.819	114
		392

The first oil up the tube is evidently absorbed by heavy material in the earth; the first oil recovered dissolves material from the earth, which increases its specific gravity beyond that of the next fraction.

Fourth Fractionation.

	(0.815)		(0.8168)		(0.819)		(0.8205)		(0.823)	
	Specific gravity.	Cubic. centimeters.	Specific gravity.	Cubic. centimeters.	Specific gravity.	Cubic centimeters.	Specific gravity.	Cubic. centimeters.	Specific gravity.	Cubic centimeters
A	0.8135	19	0.812	30	0.8115	24	0.8095	18	0.8092	35
B	0.805	27	0.8122	42	0.8127	35	0.813	26	Lost	35
C	0.8118	50	0.8165	55	0.8173	60	0.819	45	0.8195	60
	0.813	15	0.818	25	0.8185	22	0.8195	17	0.8213	25
D	0.8147	140	0.818	160	0.820	160	0.8215	130	0.8235	150
EF	0.8175	360	0.8195	305	0.8215	310	0.824	340	0.826	280
		611		617		611		576		585

The sum of the fractions of oil displaced from the earth is as a rule only about 2/3 of the volume of the oil used. A pressure of approximately 200 tons per square inch on the earth from which water has displaced all oil that it will result in the liberation of considerable water but very little oil. When earth which has been pressed is heated to 165° for three hours, considerable water distils over, but much less oil than would be expected; for example, from 75 grams of earth which should contain 25 cc. of oil only 4 cc. of oil was obtained. The earth was removed once from the flask and pulverized, and when the heat was discontinued the earth was thoroughly dry. On extraction with ether in a Soxhlet extractor the earth gave a solution having the color of the original petroleum. The extraction was continued until the extract was

To see how much of the weight of the earth used the second time was due to material which it had retained from its first use, 300 grams of earth were mixed with 300 cc. of crude petroleum and the oil displayed by water. The oil recovered measured 205 cc., and the weight of the earth after drying for several weeks at room temperatures was 347.5 grams. Fully 15 per cent., therefore, of the weight of the earth used the second time was solid matter which it had retained from its first use.

While slow geologic processes may drive out most of the water, the evidence is in favor of the view that *some* of the oil will always be left behind. Some experimental work on samples collected in the field confirms the laboratory results:

The "cap rock" of oil accumulations in Caddo Parish, Louisiana, consists of a fine-grained clay of a

considerable thickness. It has no odor of oil nor any oily feeling, in fact appears to be perfectly barren. By extracting with ether, however, a noticeable amount of petroleum is obtained of considerable greater viscosity than the petroleum supply below. The clay contains much moisture, and it is absolutely evident that it once contained more oil than at the present time. It seems, therefore, to be a case in point of where petroleum has accumulated by the capillary action of water. This seems to point out an extremely useful application of the phenomena described above.

To better compare the oils of different specific gravities that were obtained in the fourth fractionation each of six 300 cc. samples (five of partly refined oil and one of crude petroleum) was separated by distillation into ten fractions. Each sample was distilled in the same 500 cc. distilling bulb, which was heated by an electric stove that entirely surrounded it. The oil was first heated to 200° under atmospheric pressure and then to 360° under a pressure of 50 mm. The diminished pressure was obtained with a large Chapman water pump and kept constant by the use of a valve which automatically admitted air to the evacuated system whenever the pressure fell below 50 mm. This valve was constructed from a piece of iron pipe 1 inch in diameter and 5 feet long. The lower end was closed with a cap and the pipe filled with mercury to a depth of 76 cm. The upper end of the pipe was closed with a two-hole rubber stopper. In one hole was a long glass tube with the lower end beveled, which reached to the bottom of the mercury and could be raised or lowered as the barometer varied from day to day. In the other hole was a tube which passed just through the stopper and was connected on the outside with the apparatus to be exhausted. To prevent mercury from being drawn up and over into the apparatus by the air admitted, the end of the tube inside the stopper was drawn out and bent at a right angle and over this was slipped a cap made of larger tubing closed at the bottom, but having a fine opening in the side for air. This cap was about 6 cm. long and extended about 3 cm. below the end of the tube inside. If any mercury passed through this first fine opening into the cap, it would fall to the bottom without being drawn over into the apparatus or clogging the fine opening in the tube leading thereto. With this valve there was no difficulty in keeping a pressure of 50 mm. constant within 1 mm.

Each distillate of sufficient volume, which was not too viscous or partly solid, was tested as to specific gravity, viscosity, and percentage absorbed when treated with concentrated sulphuric acid (specific gravity 1.84).

Viscosity was measured by taking the time of flow of a measured volume of oil through a capillary, the viscometer used being the one described by Ostwald and Luther as modified by Jones and

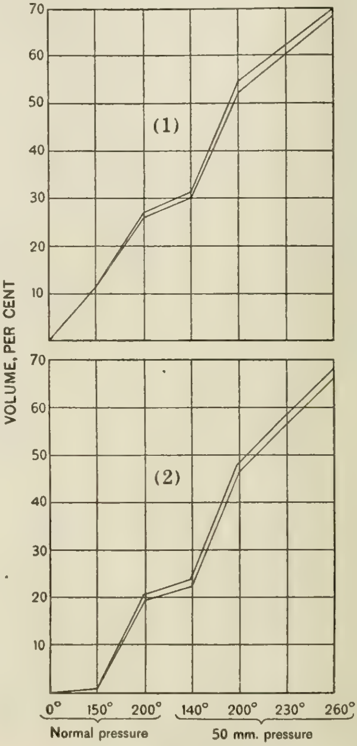


Fig. 1.

Veazey.[1] The capacity of the small bulb was 4.5 cc. and the diameter of the capillary such as to require from five to eight minutes for that amount of oil to flow through it, and 1 minute 2.6 seconds for the same amount of water. The viscosity as well as the specific gravity was always measured at a temperature of 20° C. Viscosities have been calculated from the formula $n = n_0\ TS/T_0S_0$

[1] *Ztschr. physik. Chemie*, **61**, 651.

in which n_0 is the coefficient of viscosity for water, S_0 is the specific gravity of water, and T_0 the time of flow of water through any given capillary at a given temperature; n is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as unity at any given temperatures, and T is the time of flow of the given solution at that temperature. The value for pure water at 20° was taken from the work of Thorpe and Rodger.[1]

Thirty cc. of each of these distillates where that much oil was available, or all the oil there was where the volume was less than 30 cc., were mixed with an equal volume of concentrated sulphuric acid (specific gravity 1.84) and shaken for half an hour or longer in a shaking machine. The oil and acid were then poured into a separating funnel and the acid drawn off. The oil was then washed twice with water, once with aqueous NaOH, again with water, and then with this last wash water poured into a burette and allowed to settle. After standing over-night the volume was read.

The oils boiling below 200° (at 50 mm. pressure) separated clear, but the heavy distillates were milky from water. The volume of these milky oils was read, their specific gravity was taken, and then the milkiness was removed by shaking and heating to about 60° with $CaCl_2$. The specific gravity of the clear oil was then taken and the proper correction made to the milky volume. In no case, however, was this correction large, and only for the three or four heaviest oils did it exceed one-half of 1 per cent., the largest correction of

TABLE V.—FRACTIONATION OF SIX SAMPLES BY DISTILLATION.

		1.	2.	3.	4.	5.	6.
Specific gravity		0.801	0.808	0.815	0.8195	0.824	0.810
Viscosity		0.0404	0.0555	0.0589	......	0.0657	0.0441
Tubes passed through		1	3	3	4	4	Crude oil
Normal pressure:							
Below 150°	Amount ....cubic centimeters	36	1	13	5	2	45
	Specific gravity	0.720	......	0.737	......	......	0.714
	Viscosity	0.0052	......	0.0059	......	......	0.0047
	Acid treatment: Per cent. absorbed.	4.4	......	......	......	......	8.6
	Acid treatment: Specific gravity	0.722	......	0.7365	......	......	0.712
150°–200°	Amount ....cudic centimeters	47	61	52	60	60	43
	Specific gravity	0.749	0.7465	0.756	0.757	0.759	0.759
	Viscosity	0.0075	0.0073	0.0075	0.0073	0.0072	0.0076
	Acid treatment: Per cent. absorbed.	3.4	4.4	8.2	11.3	12.0	9.3
	Acid treatment: Specific gravity	0.749	0.7469	0.750	0.749	0.750	0.752
50 mm. pressure:							
Below 140°	Amount.........cubic centimeters	10	9	3	6	10	19
	Specific gravity	......	......	......	......	......	0.7805
	Viscosity	......	......	......	......	......	0.0112
	Acid treatment: Per cent. absorbed.	......	......	......	......	......	11.9
	Acid treatment: Specific gravity	......	......	......	......	......	0.7735
140°–200°	Amount.........cubic centimeters	69	75	80	80	73	48
	Specific gravity	0.790	0.790	0.797	0.800	0.8015	0.804
	Viscosity	0.0212	0.0185	0.0211	0.0216	0.0196	0.0254
	Acid treatment: Per cent. absorbed.	3.4	4.4	8.9	9.6	14.8	11.0
	Acid treatment: Specific gravity	0.790	0.7885	0.7915	0.795	0.7915	0.799
200°–230°	Amount.........cubic centimeters	25	30	23	25	30	21
	Specific gravity	0.813	0.8135	0.818	0.8225	0.822	0.823
	Viscosity	0.0556	0.0594	0.0573	0.0661	0.0505	0.0593
	Acid treatment: Per cent. absorbed	......	4.3	11.0	8.4	10.5	8.7
	Acid treatment: Specific gravity	0.813	0.8125	0.816	0.8217	0.818	0.8175
230°–260°	Amount.........cubic centimeters	23	27	23	20	24	22
	Specific gravity	0.8255	0.826	0.830	0.833	0.838	0.8355
	Viscosity	0.1106	0.1150	0.1116	0.1168	0.1259	0.1284
	Acid treatment: Per cent. absorbed.	3.4	8.5	7.0	8.8	7.6	12.6
	Acid treatment: Specific gravity	0.8255	0.8255	0.828	0.832	0.833	0.830
260°–300°	Amount.........cubic centimeters	20	22	23	24	20	17
	Specific gravity	0.8395	0.838	Fluid	Fluid	Fluid	Fluid
	Viscosity	0.2520	......	......	......	......	......
300°–340°	Amount.........cubic centimeters	25	a30	27	30	26	25
	Specific gravity	0.847	0.849	Solid	Solid	Solid	Solid
340°–360°	Amount.........cubic centimeters	21	a26	22	......	19	20
	Specific gravity	Fluid	Fluid	Fluid	......	Fluid	Fluid
Residue	Amount.........cubic centimeters	22	17	30	45	35	32
	Specific gravity	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid
Total volume	cubic centimeters	298	298	296	295	299	292

a To 355°.

[1] *Phil. Trans.*, Vol. 185 A, 1894, p. 397.

all being 2.6 per cent. for the distillate between 230° and 260° of the oil of specific gravity 0.824. An attempt to treat with acid the oils selected to be distilled resulted in so much loss from the formation of emulsions that the loss in volume and change in specific gravity could not be determined with any degree of accuracy.

The results of the distillation of these samples are summarized in Table V.

"Fluid" means that the oil at 20° was partly solid, but would flow when the bottle was inclined; "solid" means that the oil would not change its shape when the bottle was turned upside down.

It was hoped that sulphuric acid of the strength used would dissolve only unsaturated hydrocarbons and leave untouched the paraffins and benzene. By long-continued shaking at ordinary temperatures, however, with acid of this strength benzene is dissolved, provided that the acid is in large excess. On being shaken for four hours 100 cc. of benzene were completely dissolved in 434 cc. of acid.

Three of the distillates which had been shaken with acid showed no action when treated with a mixture of equal parts of concentrated sulphuric acid and fuming nitric acid, whereas this nitrating mixture did act on distillates which had not been previously shaken with sulphuric acid. The action of the sulphuric acid, therefore, appears to have been complete.

The results of the acid treatment showed that over 90 per cent. of the oil used consisted of paraffin hydrocarbons, and that in the filtration through earth the paraffin hydrocarbons tended to collect at the top of the tube and the unsaturated hydrocarbons at the bottom.

The increasing amount dissolved by sulphuric acid in the heavier oils may be seen in the curves shown in Figs. 1 to 3. The abscissas represent temperatures and the ordinates volumes. The same distance on the x axis is taken to represent a distillate, whatever be the number of degrees over which it may have been collected. The upper curve represents the percentage of the total volume that distilled between given temperatures; the lower curve the percentage of the total volume recovered that was not absorbed by sulphuric acid (that is, the paraffin hydrocarbons). For the upper curve the ordinates are obtained by dividing the number of cubic centimeters in the distillate by the total volume of oil recovered. For the lower curve the ordinates are obtained by dividing the number of cubic centimeters in the distillate not absorbed by sulphuric acid by the total volume of oil recovered.

The area between the two curves represents the proportion of hydrocarbons soluble in sulphuric acid. It will be seen that this is greatest for the oils of highest specific gravity.

The nature of the selective action in the diffusion of oils through clays seems to be complicated.

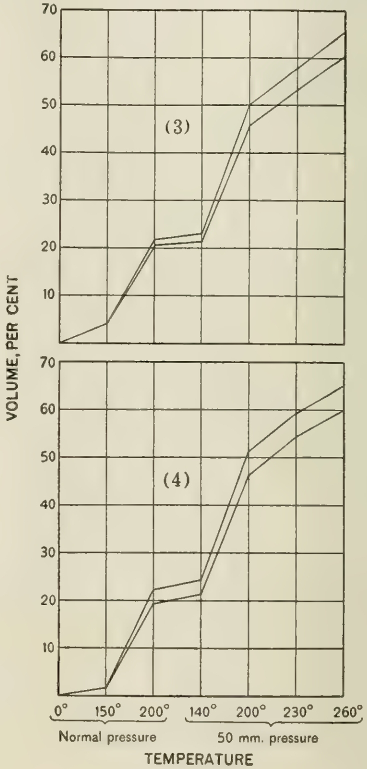


Fig. 2.

It is noticed that certain constituents of petroleum are held back with great readiness by the clay.

Such substances are, in the first place, asphalt and the sulphur compounds found in Texas petroleum. On the other hand, semi-solid paraffin is found in oils which have diffused so far through the clay as to be appreciably lighter in specific gravity. Again, it has already been shown that unsaturated hydrocarbons have a tendency to hang, that is, not to diffuse so readily as saturated hydrocarbons.

Careful study of these phenomena leads to the suggestion, as a basis for future work, that the substances in *colloidal suspension* rather than those in more perfect solution are the first to be held back.

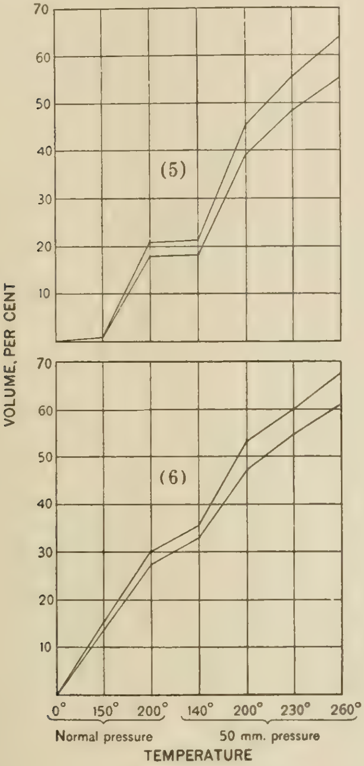


Fig. 3.

That this is particularly the case with asphaltic materials appears evident by the partially successful results already obtained by one of us, of precipitating asphalt from its suspension in petroleum by the presence of an electrolyte.

FURTHER REMARKS ON VANADIUM AND ITS ESTIMATION.

By George Auchy.

Received March 16, 1909.

An important question to the steel maker who must produce steel that will stand shock and alternating stresses is, whether or not, the earnest claim that vanadium is the best element to use to produce these qualities is a true one. Can vanadium do anything for steel that can not be done by nickel, chromium, tungsten, molybdenum, manganese, or silicon and does it outclass all these other elements in value and usefulness? The writer has made a search through the literature of the subject for an answer to this question, and while he has found an abundance of affirmative assertion, the evidence itself has been somewhat meager and contradictory evidence, that is, that bears directly on this question. Of evidence that vanadium does impart very valuable properties to steel there is no lack, and this elementary point, especially through the labors of Mr. J. Kent Smith, has received ample and complete demonstration. We need no longer ask whether vanadium is a good thing, but that it is the best thing as is so earnestly claimed, is not so clear, and as we have stated, it is to the steel maker, an interesting and important question. The writer wishes here to bring together results bearing on this point that have been quoted by him in several scattered numbers of the *Iron Age* (adding to them a few others), but expressing these results in single "quality figures" instead of in the original detailed tensile, shock, and hardness statements. These quality figures (the tensile, shock and hardness figures summed up and expressed in a single figure) were suggested to the writer by similar ones made use of by Mr. W. L. Turner in an able article in the *Iron Age* for July 2, 1908. But Mr. Turner's quality figures aim to combine only the static and dynamic properties of steel in a single figure, leaving out (perhaps properly) the hardness. Although he can not be severely (perhaps not at all) criticized for this omission, yet the general principle of his method of calculating the quality figure is obviously illogical, and his quality figures therefore are somewhat misleading. Upon reflection, it will be clear to every one that the following rule will give just results. Instead of multiplying the factors (in his method, elasticity, reduction, and alternate stress) together, as does Mr. Turner, we compare each factor separately with the same factor in some steel which we select for a standard, making the factor of the sample steel the numerator and the factor of the standard steel the denominator of a fraction. Both terms of the fraction are then divided by the least term either numerator or denominator as the case may be. Finally, after the common divisions the sum of all the numerators is

divided by the sum of all the denominators, and the result is multiplied by 100 to give a larger and more convenient figure for comparison. The standard steel need not, of course, be an actual one, but one made up of convenient round figures for the purpose. Thus for the French system, a convenient standard is elast. 50, strength 50, elong. 5, red. 5, shock 5, hardness 100, and the following example illustrates the calculation of the quality figure for a steel of 152 elast., 159.5 strength, 10 elong., 46.9 red., 0.7 shock, and 321 hardness.

$$\frac{152}{50}+\frac{159.5}{50}+\frac{10}{5}+\frac{46.8}{5}+\frac{0.7}{5}+\frac{321}{100}=\frac{3.04}{1}+\frac{3.19}{1}+\frac{2.00}{1}+\frac{9.36}{1}+\frac{1}{7.14}+\frac{3.21}{1}$$

$$=\frac{21.80}{12.14}=1.80\times 100=180 \text{ Quality Figure.}$$

But an improvement can be made by cutting out some of these factors. Thus for instance, since elongation and reduction both express the same property, to use both is to give this property (ductility) double the representation it should have. Mr. Turner therefore cuts out elongation. The writer would cut out both elongation and reduction on the ground that ductility and toughness are already represented by shock test, and these figures moreover represent perhaps not ductility at all, but nothing but the amount of pearlite (or of martensite) in the steel. Indirectly these tests are a general indication of the ductility and toughness, it is true, because pearlite interferes (and martensite still more) with these qualities also; but that there is no direct connection between elongation and reduction, and ductility and toughness, we see when we consider that ductility and toughness are qualities of the steel in its normal condition, whereas elongation and reduction are phenomena occurring after the steel has been irretrievably ruined, that is, after its elastic limit has been reached and passed.

Another factor that is of no importance and must not therefore be considered in getting our quality figures is the tensile strength, for as Mr. Turner well says, "a material is practically valueless after the stresses have exceeded the yield point." We are therefore reduced to three factors, elastic limit, shock test, and hardness, and in the results of Dr. Guillet, quoted below, the quality figures given were obtained from these three factors in the manner above described. But along with these true quality figures are also given in parentheses the quality figures obtained from all six factors, as it was thought the comparison might be of interest. In Mr. Turner's tests the quality figures are calculated from the three factors of elasticity, reduction and alternating stresses only (hardness not given) and results are therefore not comparable with the results of Dr. Guillet's tests, but only with each other.

To find then an answer to our question as to the efficiency of vanadium compared with the elements more commonly added to steel, we turn to Dr. Guillet's paper on Quaternary Steels in the *Journal of the Iron and Steel Institute* for 1906, Vol. 2, and pick out and compare vanadium nickel steels with chrome nickel, tungsten nickel, molybdenum nickel, and silicon nickel steels, using for the comparison the 3-factor (elasticity, shock, hardness) quality figures obtained as above described. Taking first quenched steels we find as follows:

Quenched Vanadium Nickel Steels.

Composition.	Quality figure.	
C, 0.20–Ni, 6–V, 0.50	258	(364, 6-factor figure)
C, 0.20–Ni, 6–V, 0.70	79	(180, 6-factor figure)

Quenched Chromium, Etc., Nickel Steels.

C, 0.20–Ni, 6–Cr, 0.50	257	(240, 6-factor figure)
C, 0.20–Ni, 5–Cr, 1.0	305	(269, 6-factor figure)
C, 0.20–Ni, 6–Cr, 1.0	268	(186, 6-factor figure)
C, 0.20–Ni, 5–Cr, 3.0	285	(305, 6-factor figure)
C, 0.20–Ni, 6–W, 2.0	285	(377, 6-factor figure)
C, 0.20–Ni, 6–W, 0.30	279	(332, 6-factor figure)
C, 0.20–Ni, 5–W, 0.30	284	(380, 6-factor figure)
C, 0.20–Ni, 6–Mo, 1.0	235	(229, 6-factor figure)
C, 0.20–Ni, 6–Mo, 0.50	284	(259, 6-factor figure)
C, 0.20–Ni, 6–Mo, 2.0	248	(237, 6-factor figure)
C, 0.20–Ni, 6–Si, 0.50	271	(364, 6-factor figure)
C, 0.20–Ni, 6–Si, 0.80	281	(380, 6 factor figure)

In the above tests, vanadium shows inferior if anything to chromium, tungsten, molybdenum, and even to cheap and common silicon. Looking for further comparisons with silicon, we obtain the following:

Quenched Vanadium Nickel Steels.

C, 0.20–Ni, 2–V, 0.30	267	(347, 6-factor figure)
C, 0.20–Ni, 2–V, 1.0	215	(261, 6-factor figure)

Quenched Silicon Nickel Steels.

C, 0.20–Ni, 2–Si, 1.5	223	(155, 6-factor figure)
C, 0.20–Ni, 2–Si, 1.0	249	(174, 6-factor figure)
C, 0.20–Ni, 2–Si, 0.50	292	(239, 6-factor figure)

Indicating again the superiority of silicon, and showing also that anything over 0.50 per cent. of either element causes deterioration.

But in the tests so far quoted, it will be seen that vastly different comparisons are obtained with the six-factor figures, this because vanadium gives as a rule such high figures for reduction of area. But further reflection only serves to confirm us

in our conviction that elongation and reduction dare not be admitted into the calculation of quality figures, where shock tests also figure, because in the first place these two tests are obviously no sure indication of ductility and toughness, as has always heretofore been taken for granted (all through Dr. Guillet's tests may be found instances of steels showing 5 or 6 times the reduction of certain other steels, and yet coming the same or even lower in shock test figures) and are therefore of no positive significance, and in the second place, if they really were an indication of these qualities, so much the greater reason why they should be omitted from the calculation, since these qualities already find representation in the shock test figures. In all the following tests of Dr. Guillet, even the 6-factor figures show unfavorably to vanadium. Considering now "normal" steels (heated to 900° C. and cooled in air) we find as follows:

VANADIUM NICKEL STEELS.

C, 0.20–Ni, 6–V, 0.30	169	(331, 6-factor figure)
C, 0.20–Ni, 6–V, 0.50	170	(320, 6-factor figure)
C, 0.20–Ni, 6–V, 0.70	182	(324, 6-factor figure)

CHROMIUM NICKEL STEELS.

C, 0.20–Ni, 5–Cr, 1.0	255	(359, 6-factor figure)
C, 0.20–Ni, 6–Cr, 1.0	217	(336, 6-factor figure)
C, 0.20–Ni, 6–Cr, 2.0	260	(303, 6-factor figure)

TUNGSTEN NICKEL STEELS.

C, 0.20–Ni, 6–W, 1.0	202	(286, 6-factor figure)
C, 0.20–Ni, 6–W, 2.0	187	(321, 6-factor figure)
C, 0.20–Ni, 6–W, 6.0	198	(338, 6-factor figure)

MOLYBDENUM NICKEL STEELS.

C, 0.20–Ni, 6–Mo, 0.50	236	(417, 6-factor figure)
C, 0.20–Ni, 6–Mo, 1.0	227	(328, 6-factor figure)
C, 0.20–Ni, 6–Mo, 2	215	(343, 6-factor figure)
C, 0.20–Ni, 6–Mo, 5.0	200	(321, 6-factor figure)

SILICON NICKEL STEELS.

C, 0.20–Ni, 6–Si, 0.50	223	(412, 6-factor figure)
C, 0.20–Ni, 6–Si, 0.80	145	(327, 6-factor figure)
C, 0.20–Ni, 6–Si, 1.0	131	(309, 6-factor figure)
C, 0.20–Ni, 5–Si, 2.0	134	(268, 6-factor figure)
C, 0.20–Ni, 6–Si, 2.0	135	(236, 6-factor figure)

Here again even silicon shows superior to vanadium, but only when the per cent. silicon is not higher than 0.50. Above that a great deterioration is manifest.

All of the results of Dr. Guillet are unfavorable we see to vanadium, but we come now to results of quite a different character, those of Mr. Turner of the Vanadium Company. In these results we must calculate our quality figure from two factors only, elastic limit and alternate stresses, hardness not being given. These quality figures are not comparable with the preceding ones.

VANADIUM CHROME STEELS.

Test No.	Quality figure.	
15	866	(713, 5-factor figure)
17	771	(699, 5-factor figure)
23	436	(443, 5-factor figure)
24	500	(550, 5-factor figure)
27	501	(534, 5-factor figure)

NICKEL CHROME STEELS.

Test No.	Quality figure.	
21	437	(559, 5-factor figure)
28	424	(507, 5-factor figure)
9	545	

These results are highly favorable to vanadium; out of 5 cases, in one only is the vanadium no better than the nickel. In two others it is well above, and in the remaining two it is very far superior to most of the nickels. But in view of the contradiction given by Dr. Guillet's results, and in view also of the fact that only one percentage of nickel (1.75 per cent.) was experimented with by Mr. Turner, and no other element than nickel compared with vanadium, we must wait for further light before drawing positive conclusions.[1] However the matter may ultimately turn out, the estimation of vanadium in steel and in alloys has become a common thing with steel chemists, who may be considered as heartily in sympathy with vanadium's struggle for supremacy on account of the ease with which the element can be estimated. The great analytical authority, Mr. A. A. Blair, first separates from the iron and molybdenum by ether, then from the nickel, chromium and copper by caustic soda, then from the alkali by lead acetate, and finally determines the vanadium by reduction with hydrochloric acid, and titration in sulphuric solution with permanganate.

Mr. J. Kent Smith, the noted pioneer in everything pertaining to vanadium, determines the vanadium at once in the iron solution by oxidation with permanganate, filtration, reduction with weighed ferrous ammonium sulphate, and titration of excess with bichromate. Mr. Chas. M. Johnson, the brilliant and original young steel works chemist, also proceeds like this, but titrates with the ferrous ammonium sulphate instead of adding an excess. The last two are obviously easy and convenient methods, but involve a filtration, and the titration in neither case is so satisfactory as a permanganate titration, so that reduction with hydrochloric acid and titration in sulphuric solution by permanganate (without separating the iron) seems preferable. In detail as follows:

[1] There are results very favorable to vanadium quoted in Harbord's "Metallurgy," but not considered here because tensile exclusively.

In steel dissolve 5.12 grams drillings in a casserole in 75 cc. nitric acid, sp. gr. 1.20. If the steel contains chromium, 25 cc. strong hydrochloric acid are also added. A blank test on the same weight of some vanadium-free drillings is also made. Cover and boil, nearly dry. If the hydrochloric acid has been added, add 50 cc. strong nitric acid, and again boil, nearly dry. Remove cover and evaporate to dryness at a gentle heat. Cover and heat (the flame barely touching the plate) to decomposition of nitrates and until cover is dry. Add 150 cc. strong hydrochloric acid and boil nearly to dryness. Add 75 cc. dilute (2 to 1) sulphuric acid and evaporate, with cover off, to complete expulsion of the hydrochloric acid. Cool, take up with 300 cc. water, and again evaporate to pastiness. This second evaporation is to give any V_2O_3 all possible chance to oxidize up to V_2O_4 in recognition of Treadwell's point that strong hydrochloric acid reduces V_2O_5 to a variable mixture of V_2O_4 and V_2O_3. Take up with 100 cc. water and heat. Transfer to a 500 cc. Erlenmeyer flask. Cool, dilute to about 350 cc. and titrate with permanganate, of iron strength 0.005585; cc. permanganate divided by 10 gives per cent. vanadium. The pink color must persist after 50 or 60 shakings of the flask. In chrome vanadium steels the permanganate used up in neutralizing the green chromium color must of course be allowed for. This may be found once for all by experiments. The writer's rule is to deduct 0.1 cc. for every 1 per cent. chromium and 0.1 additional, this for the neutralization of the green chromium color, and in addition to the regular dummy. As stated, this chromium correction may be found once for all, but not so the regular dummy. This must be made every time, or at least every time a fresh lot of sulphuric acid is used. It seems to be the sulphuric acid that is responsible for the variations in the dummy, but of this the writer cannot be sure. He has only noticed that for a long series of tests the dummy will be constant (say 1.0 cc.) and then suddenly will change to perhaps 0.7 cc. which will then persist for another series of tests and so on, so a dummy every time would seem to be safer.

In Ferro-vanadium.—Take 0.512 gram of the crushed sample, and for the dummy take 0.3 gram of any vanadium-free steel drillings. Dissolve in a dish in dilute nitric acid, adding strong hydrochloric acid. Boil nearly to dryness with cover on and add 50 cc. strong nitric acid. Boil nearly dry, lower flame, remove cover, and evaporate at a gentle heat to dryness, add 25 cc. strong hydrochloric acid and boil until green, add 50 cc. water, stir up and filter. Wash alternately with hot, dilute hydrochloric acid and water. To filtrate add 1 cc. concentrated nitric acid and 50 cc. concentrated hydrochloric acid and evaporate to dryness—at a gentle heat when nearly dry. Add 150 cc. strong hydrochloric acid and boil nearly dry. Then 15 cc. dilute sulphuric acid (2 to 1) and evaporate until no smell of hydrochloric acid is perceptible, cool, add 300 cc. water, mix, and evaporate again. Take up with water and heat, transfer to a 500 cc. Erlenmeyer flask, cool, dilute to about 350 cc. and titrate with permanganate of 0.005585 iron strength. cc. permanganate equals per cent. vanadium. The residue is tested for vanadium, by burning of paper, dissolving in hydrofluoric and a little sulphuric acid, evaporating, igniting and weighing as Fe_2O_3 plus V_2O_5. Then the V_2O_5 separated by fusion with sodium carbonate and filtration of the aqueous solution, the residual Fe_2O_3 weighed and the V_2O_5 obtained by difference.

This method of determining vanadium by reduction with strong hydrochloric acid and titration with permanganate has of course been in use from the very beginning, as it is the simplest and most obvious plan. But the general, if not the unanimous opinion has been that the iron must first be separated. From Campagne, the first one to publish a description of the method, applied to steel down to Blair, who recently has described an application of the method to steels containing molybdenum and chromium, the iron is directed to be first separated by ether. Why? The only reason the writer can see is the fact that the end point of titration cannot be distinguished with much iron present, and the liquid hot when titrated. But if the liquid be cold there is no difficulty in getting the end point of the titration. Must the liquid then be hot? The following tests with vanadium solution made in the cold seem to answer this question in the negative.

Per cent. present, by reduction with zinc to V_2O_2 form, 1.13.

Per cent. present, by mercurous nitrate method, 1.10.

Per cent. found by above described method, 1.15, 1.13, 1.15, 1.14, 1.15, 1.11, 1.13, 1.13, 1.13, 1.12, 1.13, 1.13, 1.15, 1.16.

Then a new vanadium solution was analyzed, found to contain no impurity except alkali, and the vanadium determined in an aliquot portion

gravimetrically by mercurous nitrate precipitation with the following results:

Vanadium, per cent.: 1.36, 1.39, 1.34, 1.37, 1.35, 1.36, 1.36, 1.36.

Then as above, titrating cold, per cent.: 1.35, 1.33, 1.36, 1.33, 1.29, 1.31, 1.29.

Then with iron present equivalent to a sample of steel: 1.37, 1.38, 1.39, 1.38, 1.37, 1.38, 1.36, 1.38, 1.39.

Then without iron, titrating hot: 1.37, 1.37.

The point made by Treadwell that strong hydrochloric acid reduces V_2O_5 to a variable mixture of V_2O_4 and V_2O_3 is a point that it appears has been entirely ignored by other analysts.

The above results show no indication of any such thing as declared by Treadwell, but the writer did get a series of three results—all obtained at the same time—that do corroborate Treadwell's statement, namely, 1.48, 1.52, 1.55. But evidently the error is one that occurs but rarely. To obviate it altogether, the writer can think of nothing better than to evaporate to pastiness a second time before titration, in order to give the V_2O_3 if present plenty of opportunity to oxidize up to V_2O_4. Whether or not this precaution serves its purpose, he cannot say. He has not had any high results since its adoption.

THE FORMATION OF WHITE SCALE ON STEEL AND THE SURFACE DECARBONIZATION OF PIPE-ANNEALED STEEL.[1]

By Charles Morris Johnson.

Received April 10, 1909.

When bars of steel are annealed in pipes, with charcoal, to produce a scale-free, frosted, metallic finish, there is frequently found at the surface of the metal a coarsely crystalline structure (H), (G) Fig. 2, that is much lower in carbon content than the remainder of the bar. Such steel will not harden file-proof on the outside. It is rejected for that reason by makers of twist drills, though this defect be so slight as to require a magnifying glass for its detection.

In pipe-annealing, the bars are put in a steel tube that is welded shut at one end. The spaces between the pieces are filled in with wood charcoal. The open end of the pipe is plugged with fire-brick, fire-clay and a disc of plate steel. A small vent hole is located at one end of the pipe to permit the escape of the large quantity of carbon monoxide that is generated by the reaction between charcoal and the air yet remaining in the vessel. As apparently dry charcoal often holds considerable moisture in its pores, some water vapor must also be liberated.

The superficial decarbonization (G), (H), (I), Fig. 2, is at times much more pronounced than at others. The writer became interested to investigate the process with a view to discovering the primary cause of this very objectionable feature of annealing in a closed tube.

In the first place, it was soon noted that the condition frequently exists in steel before it reaches the annealer, due to forging at too high temperatures.

Again, it was deemed possible that the scale, always existing on the steel when it is put in the pipes, might react with the charcoal to form CO_2. Further, that the latter gas would, under the existing conditions, decarbonize the steel by the reaction $CO_2 + C = 2CO$.

To test this theory some 5/8″ Rd., high carbon steel rods were placed in a porcelain tube and heated for 18 hours with a slow stream of pure, dry carbon dioxide passing through the enclosure. The following points were noted:

1st. A glittering black scale was produced on the fractured or otherwise unpolished surfaces of the bars. On fracturing the latter, a distinct ring of coarse crystals was found to exist at the margin of the fractures. This scale has a curious property of adhering in a thick, sparkling black mass on rough fractured surfaces but when polished steel is exposed, at a red heat, to the attack of CO_2, only a black discoloration resulted. The scale referred to, proved, on analysis, to be Fe_3O_4. This experiment showed that carbon dioxide may cause "bark" (surface decarbonization) but not to a marked enough extent to offer a satisfactory explanation.

2nd. Some pieces of the same bar were heated in a stream of pure, dry hydrogen. A frosted metallic surface was produced and also a slight "bark." Hydrogen, therefore, will decarbonize steel by forming hydrocarbons.

3rd. Next, a piece of the bar was heated in the closed porcelain tube, packed loosely with charcoal. First air was expelled, but, as the heat attained slight redness, large quantities of CO escaped at the outlet end. After an 18-hour heating, at about 750° C. to 780° C., a handsome frosted, metallic surface had displaced the black oxide and much decarbonization was noted. The carbon

[1] From a paper read at the March, 1909, meeting of the Pittsburg Section of the American Chemical Society.

content of the bar before annealing was 1.08 per cent. The decarbonized zone yielded but 0.84 per cent.

4th. Thinking that CO gas might be the active agent in (3), a small clay boat was filled with about a tablespoonful of charcoal. The boat was then placed in the tube with a piece of the steel and the usual period of heating followed. The result was the same as in the third experiment. *Note*: Annealing in a stream of natural gas produced a sooty exterior and a heavy "bark" (see J, Fig. 2).

5th. The fourth trial suggested annealing a piece of steel in an EMPTY, CLOSED TUBE with NO CHARCOAL or other reducing substance! No attempt was made to remove the air except as it was partially driven out at the vent end by expansion. The only precaution taken was to prevent indrawing of more air, at *any time*, while the tube was *hot*. The same result was obtained as is shown in the white bars at (C), Fig. 1, that is, an aluminum-like surface with great decarbonization underneath! This experiment was repeated with steel containing but 0.10 per cent. carbon and also with steel containing large quantities of chromium and tungsten. The 0.10 carbon steel is given at (B), Fig. 1.

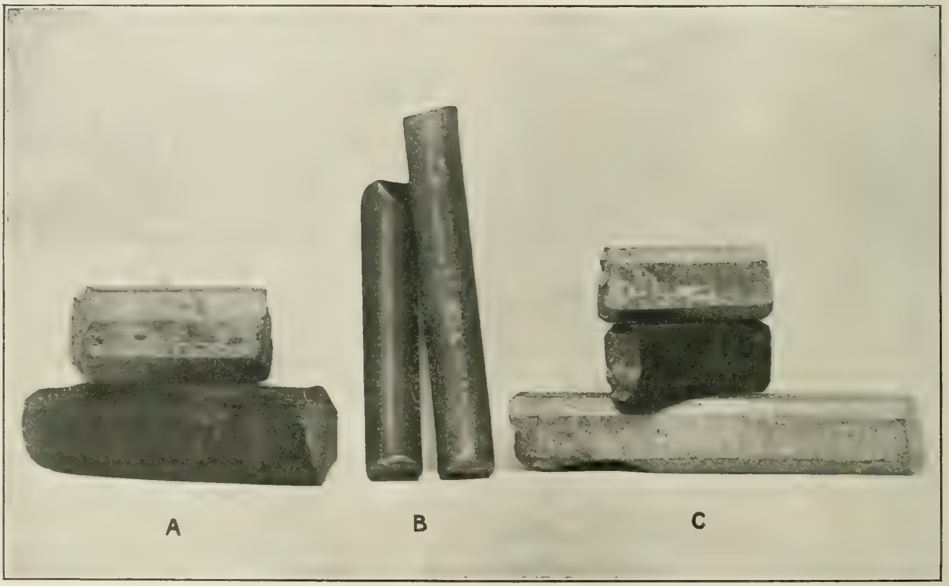


Fig. 1.

The writer felt that he had now reached the first goal and that the most active agent in surface decarbonization is the rust or scale which is actually reduced to metal at the expense of the carbon in the steel to which it adheres:

$$4C + Fe_3O_4 = 3Fe + 4CO.$$

In this connection the question arose, would steel with an extra heavy, loosely adhering scale perform in like manner? Or, in other words, Was close contact necessary for reduction? To settle this query a small piece of quarter octagon of saw analysis was given a prolonged heating in an *open* muffle at about 850° C. This treatment blistered the bar with a thick scale that was so loose that the sample had to be transferred to the annealing tube quite carefully to prevent the scale from being jarred off. After 15 hours' heating no change was noted, that is, the scale was still black. After a second heating of 18 hours the *surface* of the scale presented a slight *grayish* caste. After a third period of 18 hours' heating it was found that the heavy black scale was gone and, in its place, a *white*, loosely adhering, aluminum-like scale existed on the steel. Here, apparently, the black scale had begun to reduce on its top surface first.

This fact pointed to the existence of a reducing gas in the tube.

6th. The writer then placed a piece of high carbon steel in the tube, together with a porcelain boat containing some hard, semi-fused iron oxide obtained from a carbon combustion of steel drillings in oxygen. This hard, baked mass (D), Fig. 2, was given 18 hours' heating at a temperature of about 850–900° C. The porcelain boat was removed and found to contain, instead of a dense baked mass, a loose, friable substance, and that the volume of it exceeded the original about 2½ times. The steel that had been in the tube was then fractured. It was exceedingly tough and disclosed a heavy surface decarbonization (B), Fig. 2. The loose sponge of oxide was put back in the tube with a fresh piece of steel and given a second heating. This time the substance (E), Fig. 2, in the boat had become light gray in color and was no longer friable but was now adherent and almost sticky in its clinging fibers. This material assayed 98 per cent. metallic iron and, on being cut with a knife blade, presented a metallic luster. It occurs that here is a means of preparing pure metallic iron from pure oxide by heating it in a closed tube with a sealed vent (the writer used concentrated sulphuric acid for a seal), together with a piece of low sulphur, high carbon tool steel. Before turning off or lowering the heat it is, of course, necessary to close all vents perfectly, otherwise air will be drawn in the tube and metallic iron surfaces will lose the aluminum-like luster and become blued. Metallic iron so prepared should certainly be free of occluded hydrogen, which constitutes an objection to electrolytic iron. Some specular iron ore was ground to a red powder and then reduced to a gray powder in this way.

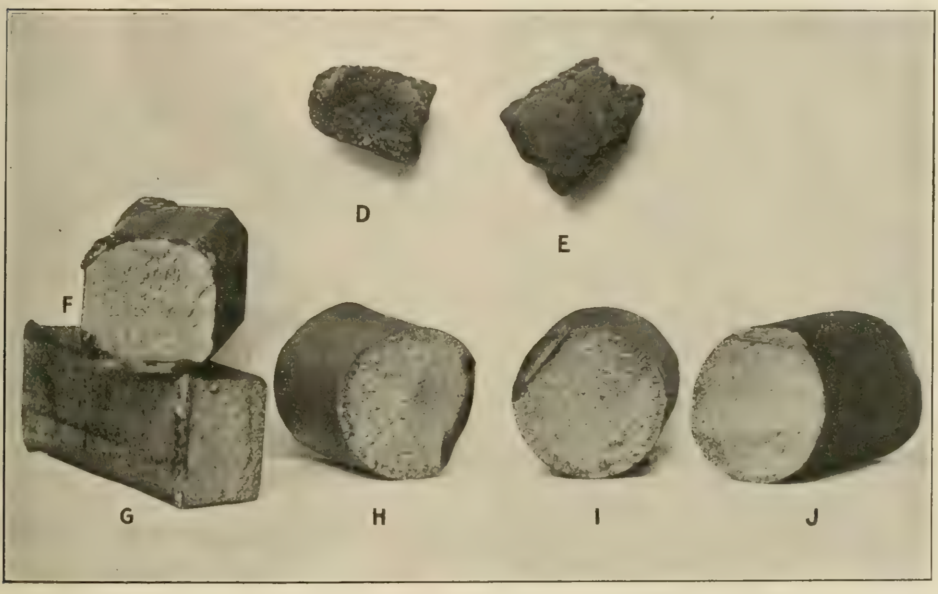


Fig 2

A piece of steel (A), Fig. 1, that had been lying in water for weeks and was covered with both black and yellow oxides was heated in an empty, sealed tube. The result was a white metallic-surfaced sample. A piece of blue steel was heated four hours in an empty tube and the blue surface was replaced by a white aluminum-like one.

7th. Further experiments developed the fact that this scale forms much more rapidly at high temperatures, that is, those above 700°. The higher the heat the more rapid the transformation from rust and black scale to the white and metallic scale. This white scale takes on the white ap-

pearance long before it is entirely reduced to metal. The author has had white scale that would be brittle and grind to a black powder. However, when the reduction is complete the scale is no longer brittle and cannot be powdered, but is entirely metallic in its properties.

8th. The corollary from the fact that white scale forms more slowly below 750° C., is that, at still lower ranges, perhaps below 650°, it may not form at all. Further experiments covering this point will be made.

9th. By annealing steel in a closed tube with a small vent to permit egress of gases but sealed against ingress of air, at temperatures close to 700° C., the surface decarbonization is so slight that no ring of coarser crystallization can be detected. Only a cupped effect can be noted around the margin of the fracture (see F, Fig. 2), yet such steel will take on a suggestion of the aluminum-like finish. Here the surface decarbonization is confined to the thinnest skin. Such steel hardens file-proof immediately under this extremely thin zone.

10th. By annealing steel that had been polished free of all rust and scale, in a tube from which ALL OXYGEN had been expelled by CO, no surface decarbonization was noted and the steel hardened file-proof. The CO was generated by heating wood charcoal.

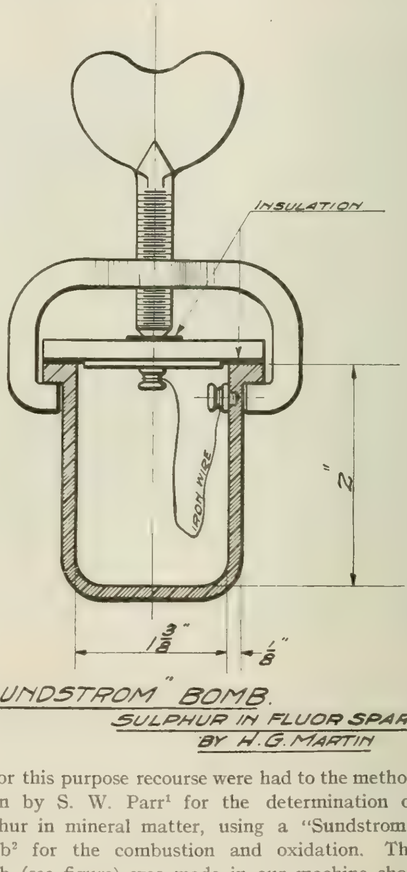
11th. A rod of polished steel was dipped in a solution of copper sulphate until it was plated with metallic copper. After heating this rod in a closed tube, *without* expulsion of the air, for a few hours, the rod was removed from the tube and was found to be coated with a handsomely appearing metallic copper. During this experiment the tube was sealed against ingress of oxygen.

BARIUM AND SULPHUR IN FLUORSPAR.

By Henry G. Martin.

Received April 29, 1909.

The author has recently analyzed samples of fluor spar containing quantities, up to ten per cent., of barium sulphate. The presence of this impurity is a more reasonable cause for condemnation of the material than either high silica or high percentage of carbonates, for while the presence of the latter substances, by lowering the content of calcium fluoride, and thereby affecting the value of the material, gives legitimate cause for argument before paying the bill, neither one proves that bane to the open-hearth furnace manager, who is seeking generally for a desulphurizing agent, which barium sulphate does. Because of the high atomic weight of barium, one per cent. of sulphur combined with it means 7.28 per cent. of the whole, while one per cent. of sulphur in combination with calcium represents only 4.25 per cent. of the whole. The determination of the sulphur alone, therefore, does not tell the whole story. It therefore became a matter of first importance to devise a rapid means of properly valuing this material while it is still on the cars.



"SUNDSTROM" BOMB.
SULPHUR IN FLUOR SPAR.
BY H. G. MARTIN

For this purpose recourse were had to the method given by S. W. Parr[1] for the determination of sulphur in mineral matter, using a "Sundstrom" bomb[2] for the combustion and oxidation. The bomb (see figure) was made in our machine shop out of seven per cent. nickel steel and was heavily nickel-plated.

[1] *Jour. Am. Chem. Soc.*, **30**, 764.
[2] *Ibid.*, **25**, 184.

The fusion mixture recommended by Parr, 10 grams sodium peroxide, 0.5 gram potassium chlorate, and 0.5 gram benzoic acid, gives entire satisfaction, working with 0.5 gram of the material, as the results below testify. A mineral having a total sulphur value of 1.61 per cent., determined by fusion with sodium carbonate and potassium nitrate, and proper removal of silica before precipitation, and a barium sulphate content of 9.80 per cent. and 10 per cent., as found by the buyer and seller, respectively, also determined by fusion with sodium carbonate, was used.

Determination number.	Sulphur, per cent.	Barium sulphate, per cent.
1.0	1.68	9.90
2.0	1.58	10.10
3.0	1.56	9.88
4.0	....	9.84
5.0	....	9.60

Sample No. 5 had one gram of sodium carbonate added to the fusion charge, with the idea that perhaps some barium might become caustic, due to insufficient carbon to render all bases carbonates, and so become caustic, and so soluble in water. This procedure evidently had no value, but neither is it likely that it caused the low result.

The details of the method follow:

The fusion charge is placed in the bomb, 0.5 gram of the mineral added and mixed by stirring, the bomb closed, after adjusting the fuse of soft iron wire, No. 31, and the latter fused with a 3.5 ampere current.

The bomb is placed in a copper dish filled with water and which is made one pole, a copper wire curved so as to have considerable spring, resting on the cover, being the other pole.

The explosion takes place very quietly. After a few minutes' cooling, the melt is washed out into a beaker with hot water and placed on a steam table until the decomposition of the peroxide is effected, or it may be boiled, but here enters the objection to boiling an alkaline solution over a gas flame, due to contamination by sulphur in the gas. It is then filtered on pulp, the filtrate acidified with hydrochloric acid and the sulphur precipitated by adding barium chloride.

The filter, with the residue, is transferred to a beaker and sufficient dilute hydrochloric acid added to dissolve all mineral matter. The determination is then filtered from the paper and the barium precipitated by adding sulphuric acid.

The excess of sulphur over that required to form the barium sulphate is calculated to calcium sulphate, and so reported, and this amount of calcium afterwards deducted from that found later as calcium fluoride.

The determination of the remaining constituents of fluorspar is made as follows:

Five-tenths gram of the material is placed in a small beaker, moistened with water and ten cc. acetic acid added (see *Chemical Engineer*, **3**, No. 2). This is allowed to stand for some time on the steam table and is then diluted and brought to a boil, and filtered on an S. & S. 589 blue ribbon paper. From the filtrate, oxides of iron and aluminum, lime and magnesia are determined as in limestone, the latter two being calculated to and reported as the carbonates. Should there be evidence of lead in the spar, it may be separated by passing hydrogen sulphide previous to precipitation of the iron and aluminum.

The residue from the acetic acid treatment is placed in a platinum crucible and after burning off the paper at a low heat is roasted for ten minutes in an ordinary Bunsen flame, and the weight registered. A few cc. hydrofluoric acid are then added and the crucible heated gently until contents are dry, then roasted again for ten minutes in the same flame as before. The difference in weights is considered silica. One cc. sulphuric acid is then added and gentle heat applied until the calcium fluoride has all been converted to the sulphate, the crucible cooled, hydrochloric acid added and the whole washed into a beaker of 150 cc. capacity and diluted somewhat. After boiling, if no barium or lead be present, there will be no undissolved residue; if there be a residue, it may generally be discarded here, after filtering. However, if so desired, ignite it and weigh as a check on the first barium determination, or if it contain lead dissolve in ammonium acetate and separate with hydrogen sulphide. Hydrogen sulphide may also be passed through the filtrate, but there will always be some platinum precipitated here, which should not be confused with lead. This filtrate is now ready for the determination of oxides, lime and magnesia. The oxides are added to the weight of those dissolved by acetic acid, the lime calculated to fluoride, after deducting such as may be required to form the calcium sulphate mentioned before, and the magnesium calculated to fluoride.

These manipulations are all on the order of the "rough and ready" kind but without using them the average works chemist would never see the end of his day's work. No claim is made for the accuracy of the silica determination for all sam-

ples but it has apparently given good results on all samples which have come under the author's notice. The two precipitations of barium sulphate are made in large bulk without reference to dissolved silica being present. All my results have checked closely with those obtained by fusion with sodium carbonate and removing silica by dehydrating and filtering, previous to precipitation. Treating the barium sulphate with sulphuric acid and hydrofluoric acid, evaporation and ignition have failed to show the presence of any silica. If lead be determined, it should be calculated to the sulphide and the proper amount of sulphur deducted from that remaining after calculating barium sulphate, before calculating the remainder to calcium sulphate.

Should the mineral exhibit evidence of the presence of iron pyrite it would be difficult to properly place all the sulphur, and a direct fluorine determination would be necessary unless one be willing to consider all the calcium, insoluble in acetic acid, as the fluoride, no sulphate being present.

The whole scheme is offered merely as a means of quickly classifying a material which heretofore has required a long time for its proper analysis.

LABORATORY OF THE LUKENS IRON AND STEEL CO.,
COATESVILLE, PA.

ADDRESSES.

SOME INTERESTING POINTS IN THE MANUFACTURE OF C. P. CHEMICALS.[1]

By J. T. BAKER

The source from which the manufacturing chemist obtains his supply of raw material and the methods employed for making the various chemical products are subjects of considerable interest and inquiry to those who have never paid much attention to the manufacturing side of chemistry. The analytical chemist who is interested only in the purity of his reagents is not particularly concerned as to their origin or method of preparation, nor is the student particularly interested, as his attention is taken up solely in experimenting with such chemicals as are placed before him. The manufacturer, however, is interested from an economical point of view and is looking for the cheapest source and the most economical methods. It is sometimes imagined by those who are totally ignorant of the nature of chemicals that there is something mysterious and uncanny about chemical manipulations and chemical preparations are imagined by them to be derived from roots and herbs or some other mysterious sources on the earth. To a certain extent this is true, for we shall not go very far in our search for a source of supply before reaching Mother Earth. The chemical manufacturer, however, especially the manufacturer of C. P. chemicals, seldom resorts the raw material as if it comes from the earth, for the greater part of his raw material is the product of other industries in which the material as found in nature is converted into a commercial product better suited to his requirements, as for instance the various metals, copper, zinc, cadmium, etc., brimstone, nitrate of soda, salt, alkalis and many other crude salts.

[1] Paper read before the Philadelphia Section, February 18, 1909.

In a great many instances it is more economical to use raw material in a partly purified form rather than to attempt to follow out every step of the preparation from the natural material to the finished product. This is especially true in the case of the manufacturer of C. P. chemicals, for his products cover a large field and include a great variety of chemicals, the demand for many of which is comparatively small, so that he is dependent to a great extent upon other industries for a large part of his supply. The chemist of old was very independent in this respect, for previous to the time that chemistry became a distinct science, the chemist sought his own raw material and prepared his limited stock of reagents himself, but as the field of chemistry enlarged and his wants increased he began to realize his limitations and became either an analyst or a manufacturer. This resulted in a division of labor and a specialization which is the condition which we find to-day. The manufacturer also, instead of attempting to cover the whole field of chemical products, takes up special lines, as commercial chemicals, C. P. chemicals, pharmaceutical preparations, etc. The division of labor and devotion to specialties seems to be inevitable, not only because the field of labor is so large and man's capabilities are limited, but because concentration of energy is necessary to gain perfection. Even in large industries where a great variety of products are manufactured, the greatest efficiency is gained by dividing the work into departments devoted to special lines.

The manufacture of C. P. chemicals is a specialty and requires a knowledge and experience peculiar to itself. While the preparation of chemical compounds is to be found described more or less in books, these descriptions are intended mainly for laboratory experiments and are seldom of practical value when working on a commercial scale. Two requisites confront the manufacturer in his efforts to keep down the cost of production, first a cheap source of supply, and second economical methods of manufacture. We are principally concerned at this time with the source of supply.

C. P. acetic acid is prepared by distilling glacial acetic acid of commerce which is the product of the dry distillation of certain kinds of wood. The commercial acid can be obtained in a number of grades of strength and purity, but the glacial is the most suitable for making C. P. acid.

C. P. arsenious and arsenic acids are prepared from the arsenious acid of commerce, obtained as a sublimed product from roasting various kinds of arsenical ores.

C. P. boric acid is prepared by recrystallizing boric acid of commerce. The latter is derived indirectly from the borax deposits in the earth, mainly from the great borax beds found in Southern California.

C. P. chromic acid is made from bichromate of potash, an article of commerce made on a large scale from chrome iron ore.

C. P. citric acid is prepared by recrystallizing citric acid

of commerce. Citric acid is the acid of the lemon and production of the commercial acid forms an extensive industry in countries where this fruit grows abundantly.

C. P. hydrochloric acid is prepared by redistilling commercial muriatic acid. Rock salt, and to some extent crystal salt, forms the basis for the manufacture of this acid, which is one of the largest products of the chemical industry. The C. P. acid is made from so-called pan acid, this being the acid made in the first part of the operation, where iron pans are used and is stronger and contains less impurities than the acid found in the latter part of the run where roasters are used. This acid cannot be made economically on a small scale, owing to the large percentage of weak and very impure acid formed, as well as the residue of sodium sulfate, for which a market must be found. Another source from which C. P. acid is sometimes made, is muriatic acid made by synthesis of chlorine and hydrogen gases obtained in the electrolytic decompositions of sodium and potassium chloride. This makes a very pure acid absolutely free from arsenic but always contaminated more or less with free chlorine.

C. P. nitric acid is prepared by redistilling nitric acid made from nitrate of soda and sulfuric acid. This acid can be made cheaply on a comparatively small scale for the reason that it does not require a very complicated apparatus, and all of the acid produced is suitable for redistilling to make C. P. acid. The nitrate of soda used is the refined product of the niter deposits in South America.

C. P. sulfuric acid is prepared by redistilling and concentrating commercial sulfuric acid. Sulfuric acid forms the largest product of the chemical industry and is produced in enormous quantities. The source from which it is made is either native sulfur, the acid from which known in commerce as brimstone acid, or from sulfur ores forming what is known as pyrites acid. For C. P. manufacture the brimstone acid is preferred, as it contains less arsenic than pyrites acid.

C. P. hydrofluoric acid is prepared by redistilling commercial hydrofluoric acid which is made from native fluorspar and sulfuric acid.

C. P. oxalic acid is prepared by recrystallizing oxalic acid of commerce. The latter is made generally from sawdust and caustic potash or soda.

C. P. phosphoric acid is made from phosphate rock or from the bones of animals. The best grades of commercial acid now being made are of a C. P. grade.

C. P. tartaric acid is prepared by recrystallizing commercial tartaric acid. The latter is made from the acid found in the grape.

The original source of the aluminum salts is principally bauxite, native oxide of alumina, although cryolite, the double fluoride of sodium and aluminum, furnishes some of the aluminum oxide of commerce as a by-product in the manufacture of bicarbonate of soda. From bauxite are made the sufate and potash alum from which are prepared the C. P. salts by recrystallization. Aluminum metal is also made from bauxite by the electric current and is the source from which are made the chloride and nitrate.

All ammonium salts originate from ammonia gas obtained as a by-product in the manufacture of coke and illuminating gas from bituminous coal. The hydrate, chloride, carbonate and sulfate are commercial products made directly from the ammonia thus obtained and from them the C. P. products are prepared by recrystallization on redistillation. All the other ammonium salts are prepared directly from C. P. ammonia by combination with acids.

All barium salts originate from witherite, the native carbonate of barium. From this the chloride and nitrate are made and purified by recrystallization. From these the other salts are made by decomposition.

Bismuth salts: Chloride, nitrate and sulfate are made direct from the metal, which is soluble in acids, and then purified. The carbonate and oxide are made from the chloride or nitrate.

Cadmium salts: Chloride, nitrate and sulfate are also made direct from the metal and then purified and from the chloride are made the carbonate and oxide.

The metals, copper, tin, iron, mercury and zinc also form the basis from which most of the salts of these metals are made.

All C. P. calcium salts are made from marble.

All C. P. chromium salts are made indirectly from bichromate of potash.

All C. P. cobalt salts are made from the oxide, an article of commerce obtained in smelting cobalt ores.

C. P. copper sulfate is prepared by recrystallizing the commercial sulfate, blue vitriol. This is the only salt of copper not made directly from the metal by the C. P. chemical manufacturer.

C. P. ferrous sulfate is prepared by recrystallizing the commercial sulfate known as copperas, the other salts being made from the metal as noted above.

Lead compounds are made from lead oxide of commerce, except C. P. acetate of lead which is prepared by recrystallizing the commercial acetate of lead.

C. P. magnesium compounds are made from magnesite, the native carbonate, with the exception of the sulfate which is prepared by recrystallizing Epsom salt.

Molybdic acid, MoO_3, is made direct from the mineral molybdenite, the native sulfide of molybdenum. The oxide is soluble in ammonia and forms the basis from which are made all the other compounds of molybdenum. This is one of the few instances where the chemical manufacturer uses the native raw material.

The principal source of all potassium compounds is the Stassfurt Mines in Germany, which yield the chloride and sulfate of commerce, from which are made the following commercial products: Nitrate of potash by double decomposition of the sulfate with sodium nitrate; chlorate of potash by oxidation of the chloride with chlorine gas, obtained by the electrolytic decomposition of the chloride in the manufacture of caustic potash; carbonate of potash from the chloride (to a limited extent), and also indirectly the bichromate, permanganate and cyanide of potash. The carbonate is also made from wood ashes and beet sugar pulp. The commercial grades of the above are the basis from which the C. P. grades are prepared by recrystallization, while all the other C. P. salts of potassium, such as the acetate, arsenate, chromate, citrate, fluoride, nitrite, sulfite and sulfide, are made by combining the C. P. carbonate or hydrate with the proper acid.

The principal source of all sodium compounds is common salt. From this source the carbonate is made either by the LeBlanc process or the ammonia soda process and the sulfate as a by-product in the manufacture of hydrochloric

and nitric acids. Cryolite, the double fluoride of sodium and aluminum, is also a source from which is made the bicarbonate of soda, and the nitrate of soda is the refined nitrate deposit of South America. From these commercial products the C. P. grades are prepared by recrystallization. C. P. sodium acetate is prepared by recrystallization of commercial acetate of soda. C. P. carbonate of soda is prepared from the bicarbonate. C. P. caustic soda is made from the chloride of electrolysis. C. P. sodium phosphate is prepared by recrystallizing commercial phosphate which is derived from phosphate rock. All other C. P. sodium salts are prepared from the carbonate or hydrate by combination with the different acids.

All C. P. strontium salts are made from commercial carbonate of strontium.

As noted above, all the salts of tin and zinc are made direct from the metal and purified by recrystallization.

THE UTILIZATION OF ATMOSPHERIC NITROGEN, PARTICULARLY FOR THE MANUFACTURE OF AIR-SALTPETRE.[1]

By Hofrat Prof. Dr. A. Bernthsen

Ludwigshafen a/Rh., Director of the Badische Anilin- u. Soda-Fabrik.

Of the two chief constituents of the atmosphere, we have hitherto been accustomed to look upon oxygen as the fundamentally important element. We are compelled to breathe it in order to support life; it is indispensable to almost every process of heating and combustion, and in the form of oxides, salts and the like, it constitutes nearly one-half of the earth's crust. Nitrogen, on the other hand, we regard as a gas which will not support combustion. We breathe it in and out without it benefitting us in any way, in fact, unless mixed with oxygen, we are unable to exist in it, and it is generally characterized by a great disinclination to enter into chemical reaction. In spite of this, however, compounds of nitrogen play such an important part in the nutrition of all living organisms, that the task of finding out and opening up new sources of nitrogen compounds, has become one of the most interesting and pressing problems of the day.

Schulz-Lupitz, one of the first of Liebig's pupils in the domain of agricultural chemistry, has written: "Nitrogen is, after water, the greatest factor in the creation, growth, and working of nature; to bind it and be its master, that is the problem, to make use of it, therein lies real agriculture, to bring its sources, which are inexhaustible, into service, that it is which creates wealth."

I propose, therefore, to occupy your attention for a short time, with the problem of the utilization of atmospheric nitrogen, a problem on which, a few decades ago, scarcely any one would seriously have thought of lecturing.

The supply of nitrogen compounds has become of particular importance to the department of agriculture, and this is a branch of national economy on which the prosperity of nations to a great extent depends, for even if a country, owing to special circumstances, develops into an industrial state, it is nevertheless dependent on progress in agriculture, if not within its own shores, then in other countries. This progress is, however, by no means such a matter of course, as was often assumed in former times.

[1] An address delivered at the Seventh International Congress of Applied Chemistry, London, 1909.

It used to be generally believed that the carbonic acid contained in the air, and continually supplied thereto from processes of combustion and putrefaction, and also from the breathing of men and animals, formed sufficient food for the plant, and for the production of starch, sugar, fats and cell walls, but Liebig investigated the ashes of plants and showed that mineral substances, in particular, potassium and phosphoric acid, also play an important part in the builiding up of plant organisms. He taught us further, that plants also derived nitrogen from the earth, in order to be able to build up the nitrogenous part of their organisms, in particular, for the synthesis of albumen, which in its turn is used as nourishment for the human and animal organism, just as much as are the carbohydrates and fats. Consequently, the necessity arises, not only of returning to the earth in the shape of manure all the products of decomposition and other changes of living matter (this had been carried out empirically for a long time, and in China was even enforced by law), but also of adding an extra supply of potassium and phosphoric acid salts, and of nitrogen compounds to the ground. It is true that the soil can yield crops for many years in succession, even when no such additions be made. This is especially the case if the cultivation be not forced too much, and if a suitable rotation of crops be followed, but if greater demands are made on the earth, sooner or later the fertility diminishes, and the soil finally becomes exhausted.

Liebig, who is the founder of modern agricultural chemistry, ascribes the decline of civilized nations from the height of their prosperity, to the robbery of the soil, and to the ignorant and unscrupulous using up of its treasures, without any regard to the possibility of exhausting them. He says: "Both the rise and decline of nations are governed by the same law of nature. The deprivation of the soil of its conditions of fruitfulness brings about their decline, while the maintenance of such conditions leads to their permanence, prosperity and power." He goes on to say: "The nation is not fed by peace, nor destroyed by war, these conditions only exercise a temporary influence on it. It is the soil on which man builds his home, which is instrumental in holding human society together, or dispersing it, and in causing nations and empires to disappear, or to become powerful. The absolute fruitfulness of the ground is independent of mankind, but he possesses the power of diminishing or prolonging such fruitfulness."

In Liebig's treatise on the relation of organic chemistry to agriculture and physiology, which appeared about seventy years ago, he protested most strongly against the way in which the English wasted manure through their method of sewage canalization. This treatise, however, although it created a tremendous sensation throughout the whole civilized world, was not at all well received by the landowners of that period.

We, who long ago absorbed Liebig's precepts into our very flesh and blood, find it difficult to understand how great the opposition was, which was then raised against them. In his excellent biography of Liebig, which has recently been published, Volhard describes, in a very interesting manner, the battle waged, and the reason of its failure at the commencement. He mentions, as a symptom of the feeling then prevalent, that an English agricultural paper even refused to print a correction sent them by Liebig himself. Since the end of the fifties, however, Liebig's teach-

ings rapidly acquired a band of enthusiastic followers. Liebig foresaw that, just as in his time "chemical preparations were used for healing fever and goitre," so, in the future, manure for the fields would be manufactured in chemical factories. This prophecy has been amply fulfilled. The potassium salts used are obtained from the deposits of the valuable German potash works in and around Stassfurt. The phosphoric acid, although used to some extent in the form of guano, is applied also as bone ash, or superphosphate, and in the form of the basic Bessemer slag which is particularly rich in phosphorus, and as the mineral phosphorite. Finally, in order to supply nitrogen to the soil, we use both ammonium sulphate from the gas and coke factories, and also saltpetre which is imported from Chili.

The importance of these different artificial manures is shown by the fact that in the year 1906 Germany used £15,000,000 worth. Of this sum nearly £3,000,000 were spent on ammonium sulphate, £6,000,000 on Chili saltpetre, while the remainder went on basic slag and superphosphate, potassium salts, guano, and the like. The supply of the nitrogen compounds which I have mentioned, is much more important than is the supply of the potassium and phosphoric acid compounds. The ground may be well treated with other plant foods, but it is all to no purpose if the necessary nitrogen compounds are missing. These latter have a special importance of their own, since, as Lawes and Gilbert showed, not only do they act as fertilizers, but they also play a part in assisting the plant to take up other kinds of food. The enormous influence of nitrogenous manure is shown by the following figures. According to Wagner's experiments carried out in Hessen, the yield of oats went back 17 per cent. when phosphorus was omitted from the manure, 19 per cent. when potassium was omitted, but when nitrogen was left out the yield fell by no less than 89 per cent. The average of all his experiments, carried out over a period of several years, showed that the profit per year and per hectar amounted to

*M*96 when complete manure was employed,

*M*62 when potassium was omitted from the complete manure,

*M*48 when phosphoric acid was omitted, and only

*M*5 when the nitrogenous compounds were left out.

Such facts as these prove the necessity of supplying special nitrogenous matter to the soil, and this appears all the more surprising, when we consider that theoretically a plant should be able to absorb nitrogen from the unlimited quantity at its disposal in the air, just as easily as it is able, under the influence of light, to assimilate the carbonic acid contained in the air.

It has been known, however, for a long time, that plants, in general, have not this power; on the other hand, it is true that plants do profit indirectly by atmospheric nitrogen, even if only to a very slight extent. In the first place, the electrical discharges, which take place in the air, cause the nitrogen and oxygen to combine and lead to the formation of nitrates and nitrites, which are thus continually being supplied to the soil. It has been estimated that, in this manner, up to 12.5 kg. of combined nitrogen are supplied yearly to each hectar of land in this latitude (= 11 lbs. per acre). In those parts of the tropics where thunder storms are frequent, the quantity is greater. And then again, although the actual plants themselves are unable to assimilate nitrogen directly from the air, we know from the celebrated researches of Hellriegel and Willfahrt, carried out in 1886, that leguminar plants, such as peas, beans, vetch, clover, and lupines, are able to absorb nitrogen directly from the air. The peculiar nodules on their roots, which were known even to Malphigi in the year 1687, contain colonies of bacteria, such as Bacillus radicicola and others, which have the property, otherwise seldom met with, of fixing atmospheric nitrogen, and conveying it to the plant. Several recent attempts to supply combined nitrogen to the soil have been based upon this property, and it has been suggested to supply cultures of the bacteria to the soil. Of course the old-fashioned custom known as "rotation of crops" is also founded on this property, although it had not been discovered at the time the custom came into existence, and the same remark applies to the alternative custom of raising some leguminar crop every few years, on ground which is otherwise used for raising corn crops, and eventually ploughing such leguminar crop into the ground as green manure. In this way, a rotation of crops tends to enrich the soil again with nitrogen, and such sources of nitrogen may suffice to support vegetation for a long time on virgin soil, for instance, in the tropics. If however, as is generally the case, the soil be more intensively cultivated, even supposing all the animal and vegetable refuse be used up as manure, it has been calculated that only from about 30–40 per cent. of the total amount of nitrogen required is thus supplied, so that considerable quantities of artificial nitrogenous manure are still necessary. The amount required, however, is rendered still greater, since by no means all of the combined nitrogen contained in the body of the plant returns to the soil.

Quite apart from the enormous loss brought about by the present system of sewage disposal, huge quantities of combined nitrogen, which have been stored up during countless ages in our coal deposits, are set free during the processes of combustion and putrefaction, and are thus lost to the soil. Then again, large quantities of combined nitrogen are used up in the form of nitrates, in the production of gunpowder and other explosives, and when these are fired off, the nitrogen is set free in the elementary state. It was this waste of combined nitrogen, that led Bunge to arrive at the paradox, "every shot destroys life, even if the bullet does not hit the target."

The absolute necessity and the fundamental importance of supplying combined nitrogen to the soil, either in the shape of ammonia salts, or as saltpetre, becomes consequently all the greater. According to Bertrand, the assimilation of ammonia by the soil is dependent on several conditions, which do not come into consideration in the case of saltpetre. It is generally assumed that, before ammonia can be taken up by the plant, it is converted into nitrates, by the action of the bacteria in the soil, or is in any case assimilated only with great difficulty, while the conversion into nitrate appears to be not quite complete, some of the nitrogen being set free. Moreover, ammonium sulphate is retained longer in the soil, and, in its action, is slower and less uniform than saltpetre. In order to obtain the best results, it should be applied to the soil before the seed is sown, whereas saltpetre should be strewed on the ground during germination. It is pretty generally agreed that the nitrogen contained in ammonia is only nine-tenths as valuable as

the nitrogen in saltpetre, and Wagner states that, when used on a large scale, this proportion sinks to 75 per cent. The quantity of saltpetre used per year is more than three times as large as that of ammonium sulphate.

We will now consider the future possibilities of producing these two sources of combined nitrogen, namely ammonia and nitrates.

Practically all the ammonium salts in commerce are obtained as by-products, during the conversion of coal, and similar substances, into gas and coke, whereby, however, only a small percentage of the nitrogen contained in the coal is recovered as ammonia. At the present time, the 26,000,000 tons of coal employed annually for this purpose in Germany yield only about 260,000 tons of ammonium sulphate, valued at £3,250,000. In 1906, the quantity produced was 235,000 tons, and of this 197,000 tons came from the coke-ovens, and the rest from the gas works. Five times this quantity could be produced in Germany alone, if all the coal consumed there (amounting in 1907 to 143,000,000 tons) were converted into coke, and this quantity could be again trebled or quadrupled, if rational methods were used to convert the nitrogen into ammonia, for instance, by using Mond's process for converting coal into water-gas by means of steam. Such an increase, however, is not likely to take place, because the production of ammonia will probably never be the main object, but will always be dependent on the increase in the production of coke and gas. The same reasoning applies to the calculations, which have recently been made, as to the quantities of nitrogen obtainable from the refuse yielded by washing coal, and from peat, although the possibility has been advanced of obtaining a profit, by working up the large quantities of peat found in North Germany, and elsewhere, and producing nitrogen compounds, in addition to gas for power purposes. Frank has obtained 40 kg. of ammonium sulphate from 1 ton of peat, so that the German peat bogs should yield theoretically 360,000,000 tons of sulphate of ammonia.

The second and most important source of combined nitrogen is Chili saltpetre, or sodium nitrate. To-day it sounds incredible, but it is a fact that the first ship-load which arrived at Hamburg in 1825 was thrown into the sea, because no one knew what to do with it. The export from Chili for agricultural purposes only began to assume considerable proportions at the beginning of the sixties, but since then it has grown so rapidly that at present nearly 2,000,000 tons are used annually. The actual quantity in 1908 was 1,730,000 tons, possessing a value of more than £17,500,000 and of this, Germany alone took one-third, that is, about 600,000 tons, and employed three-quarters of it for agricultural purposes, while the remaining quarter was used up in the chemical industry, for making nitric acid, explosives, aniline dyes, azo dyes, indigo, celluloid, and so on. The yearly increase in the world's consumption averages at least 50,000 tons, and last year amounted to 72,000 tons.

Considerably more than this, however, is required. It has been estimated, that, if Germany doubled the amount of nitrogenous manure applied to its soil, it would not only be able to raise all the corn and potatoes it required for consumption, but would also be able to export large quantities.

A further point to be considered is that countries of which the soil was hitherto considered inexhaustible, or the chemical industries of which are developing rapidly, are now commencing to use saltpetre in larger quantities. As an instance, I mention the United States of America, where the quantity imported has risen during the last ten years, from 100,000 tons to 400,000 tons.

Unfortunately, nature has only provided us with a comparatively restricted supply to meet this great demand. Limited quantities, arising from the action of bacteria on animal excrement, have always been found in various places, such as India; further, some has been found near the Death Valley in California, and deposits are also reported to have been found in the Sahara desert, close to the Tuat Oasis, but the only deposits which it pays to work are those in Chili, which up to 1879 were in possession of Peru and Bolivia. The saltpetre district (Pampa Salitrera) stretches from the 19th to the 26th degree of latitude, and in particular covers the eastern parts of the hill country, reaching towards the Pampa de Tamarugal and the Atacama deserts. It is from 35–45 miles from the coast and from 3,000–5,000 feet above the sea-level. The saltpetre is not found in a pure state, but is contained in the mineral caliche, and this is covered by a crust or "costra," varying in thickness from 1 1/2–9 feet. The caliche has to be extracted with water, and the solution is then evaporated till the saltpetre crystallizes out. These operations are simple enough in themselves, but the scarcity of water, labor and fuel in those regions rather complicate matters.

Up to 1905, about 62 companies had been formed for the purpose of working the saltpetre deposits in Chili, and they had a total capital of about £23,000,000. The State has imposed an export duty on saltpetre, and this brings in over £4,250,000 annually. This is considerably more than one-half of its total income from all sources. The cost, f. o. b., is from £7: 5s to £8: 10s per ton, and the average profit is estimated at about £1: 2s.

Some of the deposits, in particular those in Tarapaca, are more favorably situated and are richer in saltpetre than the others, and consequently yield a bigger profit, but it is just these rich deposits, which are rapidly approaching exhaustion. Those of Tarapaca will be worked out in about nine years' time.

Several estimates have been made of the total quantity of saltpetre still in Chili, but of course these are only approximate, and they also vary according to whether or not deposits are taken into consideration, which, by reason of the paucity of their nitrate, and their relative inaccessibility, could not be worked at a profit, unless the price of saltpetre were considerably increased. It is interesting to compare the different estimates. The most reliable figures vary from 120,000,000 tons down to 65,000,000 or even 50,000,000 tons, whereas the estimate of the Delegacion Fiscal in 1908 ran up to 223,000,000 tons. Now if the consumption of saltpetre continue to increase annually by at least 50,000 tons (and we must assume that this will be the case), 90,000,000 tons will be used up in 33 years, *i. e.*, by the year 1942, while 120,000,000 would last for 42 years, and 50,000,000 tons only for 21 years.

The price of saltpetre has been tending to rise for several years. In 1900 it cost £8: 7s per ton, in 1902 £9: 3s, in 1904 £10: 3s, and in 1908 £10: 7s. In 1906, the price even rose for a short period to £11: 11s per ton. Since 1908 it

has fallen a little. Owing to the lack of labor, wages have risen 25 per cent. since 1892, and there seems no possibility, at any rate for the near future, of the cost of production and the selling price in Europe becoming cheaper, even should the method of transport be improved.

Sir William Crookes, in his treatise entitled "The Wheat Problem" published in 1899, taking into consideration these facts, and also the continually increasing population of the world, prophesied that the supply of saltpetre would be exhausted before very many years had passed, and he described the situation as of far greater importance, than the possibility of the British coal-fields becoming exhausted. He even calls it an impending catastrophe, and points out, that, although details perhaps cannot be foretold, yet some of the immediate consequences are sufficiently apparent. In the year 1935 there will be such a demand for wheat, that, even if all the ground now available be planted, the yield per acre must be increased from 12.7–20 bushels, in order to supply it. To obtain this result, however, 12,000,000 tons of saltpetre will be required annually, over and above the 1,750,000 now being used. In other words, even if we could assume that in 1935 Chili would still possess 50,000,000 tons of saltpetre to dispose of, this quantity would be used up in four years.

We can consequently appreciate Crookes when he says: "The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists. It is certainly deeply important in its practical bearings on the future welfare and happiness of the civilized races of mankind."

We will now consider to what extent this problem has been, and is at present being solved. Quite a number of celebrated chemists have been working for some time past, on the fixation of atmospheric nitrogen, all of their experiments being instigated by the fact that the air can supply us with such enormous quantities of nitrogen. We know that the quantity of air which rests upon 1 square inch of the earth weighs 15 lbs. and that four-fifths of this are nitrogen, consequently the total nitrogen of the atmosphere amounts in round figures to four thousand billion tons. On the other hand, about 300,000 tons of nitrogen are at present used up annually in the shape of saltpetre. Consequently, reckoning on the basis of the present annual consumption, even if none of the nitrogen were replaced, there is sufficient in the air for the production of fourteen thousand million years' supply of saltpetre.

The different methods employed in the fixation of atmospheric nitrogen can be divided into three groups: First, the direct formation of ammonia from its elements, nitrogen and hydrogen, both of which have to be isolated for the purpose

The second group covers those processes in which the nitrogen is first isolated, and then converted into metallic nitrides and cyanogen compounds, which, in their turn, can be subjected to chemical reaction, and lead to the production of ammonia.

The methods of the third group aim at the direct oxidation of atmospheric nitrogen, and the conversion thereof into nitrates and the like. In this case the air itself is used directly, and a previous isolation of the nitrogen is unnecessary.

It is not difficult nowadays to obtain nitrogen from the air; several methods can be employed on a large scale. One method consists in passing the air over red-hot copper, which retains the oxygen forming copper oxide. This latter has of course to be reduced again, and the reduction can be carried out by passing generator gas over it, and it is then able to absorb a fresh quantity of oxygen from the air. An alternative method consists in liquefying air according to Linde's process, and then separating the nitrogen from the oxygen by fractional distillation. Such processes however, always increase the cost of the total operation to a greater or less extent. Hydrogen can also be obtained without great difficulty, since it results as a by-product, for instance, during the electrolysis of potassium and sodium chloride, but here again its cost depends upon the price which can be obtained for the other products of the electrolysis, namely chlorine and the alkali.

Turning now to the direct combination of nitrogen and hydrogen, we are at once met by great difficulties, since, at the high temperature at which the combination takes place, the reverse reaction also sets in, and the ammonia formed is to a great extent decomposed back again into its elements. Consequently only a small fraction of the gases can be converted into ammonia, while the rest remains unchanged. The problem certainly presents many interesting features.

The second group of methods of fixing atmospheric nitrogen depends on the property of nitrogen of combining with certain metals, to form nitrides, or with metals and carbon to form cyanogen compounds, either simple or complicated. These nitrides and cyanogen compounds are then made to undergo a further chemical reaction, and give rise, on the one hand to ammonia, and on the other hand to metallic oxides and carbonic acid or other carbon derivatives. These methods consequently bring about an indirect synthesis of ammonia from its elements. The intermediate products formed during the reaction are sometimes of such importance, that they are manufactured in this manner, without being finally worked up for ammonia. I refer in particular to the cyanides, especially potassium cyanide, which is used in great quantities in the extraction of gold from its ores.

Bunsen discovered, nearly seventy years ago, that potassium cyanide occurs in blast furnace gases, and further, that it could be synthesized from atmospheric nitrogen, carbon and potassium compounds, and even at that time, he caused experiments to be made at Grenelle, and later at Newcastle, to determine if this reaction could be developed on a large scale. It was found to be unprofitable, at any rate under the conditions then existing. Marguerite and Sourdeval found in 1863, that if barium compounds be used instead of potassium compounds, analogous results are obtained, but the reaction proceeds more easily, so that if nitrogen be passed over a mixture of carbon and barium carbonate at red heat, large quantities of barium cyanide are obtained, and this on suitable treatment yields ammonia, while at the same time barium hydroxide is generated, and can be used over again instead of the carbonate.

Another metal, which has the power of fixing gaseous nitrogen, is titanium, as was first pointed out by St. Claire-Deville and Wöhler in 1857. Either titanium nitride is formed, or, if carbon also be present, titanium cyanonitride, and these compounds resemble the cyanides of the alkaline earths in being easily convertible into ammonia, while at the same time titanium compounds are regenerated, and can be used for the absorption of fresh quantities of nitro-

gen from the atmosphere. Both these processes have recently been investigated at the Badische Anilin- u. Soda-Fabrik.

Frank, in Berlin, and Nikodemus Caro, in Lodz, working in collaboration with Rothe, in Hamburg, noticed that when nitrogen was made to react with carbon and barium carbonate, or with barium carbide, some barium cyanide was formed, but at the same time large quantities of another body were obtained, which differed from barium cyanide in containing a smaller proportion of carbon. This body is barium cyanamide. The matter was then taken up by the Cyanid-Gesellschaft, which was formed for this purpose by Siemens & Halske, the Deutsche Gold- und Silber-Scheide-Anstalt and Dr. Frank. Pfleger had suggested that the barium carbide be replaced by calcium carbide, which can be so easily obtained by heating lime and charcoal in an electric furnace. On carrying out this suggestion, however, the investigators were surprised to find that the product contained no calcium cyanide at all, but that it consisted chiefly of calcium cyanamide, mixed with graphitic carbon. The raw product contained lime and carbon as impurities; it was black in appearance and had an unpleasant odor, but the chief point was that it contained 20 per cent. of fixed nitrogen. The preliminary production of calcium carbide was subsequently found to be unnecessary, since similar results could be obtained by starting directly with a mixture of lime and carbon. The product is now generally known by the name "Kalkstickstoff" or nitrolime.

A similar product, the so-called "Stickstoffkalk," was obtained by Polszenius by carrying out the process in the presence of small quantities of calcium chloride, which had the effect of causing the reaction to take place at a lower temperature. Certain other salts possess a similar influence.

The cyanamides, on being treated with superheated steam, are split up with the formation of ammonia, and so this constitutes another process for the indirect synthesis of this compound. Kalkstickstoff or nitrolime has an additional interest, since other compounds such as the alkali cyanides, urea, and dicyandiamide can be prepared from it, and it can further be employed for case-hardening steel as well as being used itself as a manure. In the latter case, after being applied to the ground, it is acted upon by bacteria and the like, giving rise to ammonia, and consequently, like the ammoniacal manures, it must be applied to the soil before the seed is sown, otherwise serious damage can be done to the crops. According to published researches it can only be used on special kinds of soil, such as heavy absorbent soils. It is not suitable for vegetable soils and high moorlands. It also produces different effects on the various classes of plants. The figures as to the quantitative results produced by cyanamides vary to a considerable extent. Wagner has come to the conclusion that the farmer should not pay for the nitrogen contained therein, more than 80 per cent. of the price paid for an equal weight of nitrogen in the shape of Chili saltpetre, or in the saltpetre obtained from the air. In making these calculations he has taken into consideration that saltpetre is much easier to use and control.

Great hopes have been laid on the further development of these processes, and an industrious agitation has led to quite a number of companies being floated; most of the factories though are still in the state of construction, and at present it is too early to prophesy what success this industry will meet with. It will also still have to be decided whether the nitrolime is entirely suitable for application to the soil as such, or whether it will be advisable to convert it first into ammonium sulphate, and in this case how much of the profit will disappear in carrying out this further step. It is interesting to learn that at Piano d'Orta, at the first nitrolime factory erected, a plant has already been put down for converting it into ammonium sulphate, instead of using it as manure, and, according to recent reports, other works are following this example.

The third method of bringing nitrogen into a state of combination, suitable for use on a practical scale, consists in converting it by direct oxidation into oxides of nitrogen, which are then transformed into nitric acid and nitrates. Although, as I mentioned before, nitrogen shows little tendency to enter into chemical reaction, it can, under certain conditions, be made to combine with oxygen. The first compound formed is nitric oxide, NO, a colorless gas containing equal atomic proportions of nitrogen and oxygen. On mixing it with oxygen or air, it assumes a yellowish red color, owing to the formation of a higher oxide of nitrogen, which is termed nitrogen tetroxide, or nitrogen peroxide, and which possesses a constitution corresponding to the formulae NO_2 or N_2O_4. This is then converted into nitric acid, or into some other form suitable for practical purposes.

The direct combination of nitrogen and oxygen is brought about by means of high temperatures, but the degree of combination is limited by the fact, that the same temperature which brings about the formation of nitric oxide also tends to decompose it back again into its components. For every temperature, there exists a definite state of equilibrium between the oxide of nitrogen formed, and the unaltered mixture of nitrogen and oxygen, and the quantity of nitric oxide, produced at any given temperature, cannot exceed that corresponding to the state of equilibrium for this temperature. Only at a temperature under 1200° C. is nitric oxide stable against the action of heat, but, at this temperature, the amount formed is exceedingly small. Even at 1500° C., only one-tenth per cent. of the nitrogen in the air is converted into nitric oxide, and a very much higher temperature is necessary to bring about a reasonable degree of oxidation. Muthmann and Hofer, and especially Nernst and his pupils have closely studied the course of the reaction, and from their results it appears that at a temperature of 2200° C. the gases contain 1 per cent. of nitric oxide, at 2571° C. they contain 2 per cent., at 2854° C. they contain 3 per cent., and at 3327° C. they contain 5 per cent. The equilibrium constant is given by the equation

$$K = \frac{C^2_{NO}}{C_{O_2} . C_{N_2}}.$$

From the figures I have just quoted, it is apparent that, in order to be able to work profitably, the air must be heated to as high a temperature as possible, and then cooled down again with the utmost rapidity, so that as little opportunity as possible is given, for the nitric oxide, formed at the high temperature, to decompose back again into its elements.

Many methods have been, and are still being proposed, in which the air is raised to a sufficiently high temperature by the combustion of suitable materials, and Pawlikowsky,

Häuser, Brünler, Ketteler and others have paid special attention to experiments in this direction. All the methods proposed, however, suffer, on the one hand from the difficulty of obtaining a really high temperature, and on the other hand from the fact that the oxides of nitrogen formed are mixed with enormous quantities of the other products of combustion, especially water vapor, and consequently, the concentration of the nitric oxide is disadvantageously affected, and the difficulty of cooling the gases with sufficient rapidity is greatly increased. Haber's process, which consists in burning carbon monoxide with air under pressure, and thus attaining a high temperature, belongs to this class of reaction, but appears to be an improvement, since the formation of water is avoided.

The second method of bringing about the combination of nitrogen and oxygen is by the use of electricity. As long ago as 1781, Cavendish noted that when hydrogen was burned in an excess of air, the water produced was not pure, but contained nitric acid. He first made this discovery public, however, three years later, about the same time as Priestley discovered it and made it known. In 1785 Cavendish showed that all the nitrogen contained in a given supply of air could be transformed into oxides of nitrogen, by adding the necessary quantity of oxygen to it, and supplying sufficient energy in the shape of electric spark discharges. The combination of the gases can be easily shown experimentally in a eudiometer tube, over a liquid containing blue litmus; on passing electric sparks through the air enclosed in this tube, the liquid rapidly turns red, owing to the formation of nitric acid.

It is generally accepted that electricity brings about the reaction by means of the high temperature produced, but on the other hand, it is possible that it exercises also a specific electrical action on the gases, for we know that nitric oxide is produced from its elements by the action of silent discharges, as well as by the action of spark discharges and electric arcs. I have already referred to the part played in nature by atmospheric electricity, and will now turn more particularly to the results obtained by artificial means. All efforts in this field have been applied to the production of series of sparks or of electric arcs, and during the last decade, an intense activity has been developed, both in the laboratory and also on the practical scale. I should like to refer here to the labors of Crookes and Lord Rayleigh, both published in 1897, then Lepel, Guye and Naville, MacDougal and Howles, Kowalsky and Moscicki, Brode, Pauling, Le Blanc and Nürenen, Birkeland and Eyde, and Schönherr. The different companies which have taken up work in this direction include the Genfer and Freiburger Studien-Gesellschaft, the Atmospheric Products Company at the Niagara Falls, the Norsk Hydroelektrisk Kvaelstof-Cie, the Badische Anilin- u. Soda-Fabrik, the Salpetersäure-Industrie-Gesellschaft of Gelsenkirchen, and others. I propose only to take the most important of them, dealing particularly with the steps which led up to the processes now in use.

One class of scientists started by assuming that in order to use up the electrical energy to the best advantage, it should be distributed over a large number of small sparks or arcs. Bradley and Lovejoy founded their process on this assumption, and the Atmospheric Products Company was floated towards the end of last century, with a capital of one million dollars, and carried out their process at Niagara, making use of power obtained from the Falls. They employed iron cylinders about 4 1/2 feet high and 4 feet in diameter. In the axis of each of these a steel shaft rotated, containing, mounted one above the other, twenty-three zones of electrode arms, each zone containing six arms, and each arm being provided with a platinum sparking terminal. The wall of the iron cylinder formed the other electrode, and was provided with a similar number of platinum terminals or poles, situated opposite to the terminals of the rotatable electrode. When the shaft was put into motion, the electrode poles, attached to the ends of the arms, came within sparking distance of the poles on the cylinder, and sparks sprang across from one pole to the other. As the motion of the shaft continued, the electrode poles were separated from one another, and the arc was drawn out and finally snapped, only to be formed again as soon as the next pair of poles came within sparking distance of each other. A direct current of 10,000 volts was employed and no fewer than 414,000 arcs or sparks were formed and extinguished every minute. Air was passed through the cylinder, and so came into contact with a great number of arcs, each characterized by great length and extreme thinness, and consequently the air was enabled to attain rapidly the high temperature which is so necessary for the reaction, and was also cooled down again with great rapidity. According to Muthmann, the yield amounted to 430 kg. saltpetre per kilowatt-year; this yield, however, was somewhat small, and, coupled with the complexity of the apparatus as well as its initial expense and the expense of keeping it in order, sufficed to prevent the process being worked at a profit. The plant was closed down in the summer of 1904.

The first practical success in this direction was obtained, in 1903, by Professor Kristian Birkeland in Christiania, who worked in collaboration with the Norwegian engineer, Samuel Eyde. The details of their method were first published by Edström, in a lecture held in 1904, before the International Congress of Electricians at St. Louis. Otto N. Witt also described the process in a lecture given at the opening of the new Industrial-Chemical Institute of the Technical High School at Charlottenburg, and Birkeland himself lectured on it before the Faraday Society in London in 1906. It was already known that if an electric arc, fed with an alternating current, be made to burn between the poles of an ordinary magnet, or of an electro-magnet which is excited by a direct current, the arc assumes the form of a disc. More correctly speaking, the arc is blown into a half-disc at every half-period, but the impression on the eye is that of a quietly burning disc, like the sun. Birkeland and Eyde enclosed this in a flat iron-clad furnace of fire-proof clay, and passed a strong current of air through it, and they thus obtained considerable yields of oxides of nitrogen, so that the prospects of being able to work their process on the technical scale appeared very bright. Since their first experiments, the furnaces have gradually been increased in size, until those now used are so large, that each of them is fed with 700 kilowatts at a tension of 5,000 volts, and the disc of flame is over two yards in diameter. Each furnace uses up nearly 1,000 h. p., that is, one hundred times as much as those of the Atmospheric Products Company. The utilization of this large quantity of electricity in a single discharge constitutes the great difference between Birkeland and Eyde's process, and those of earlier experimenters,

who all attempted to make use of a very small current for each separate discharge, while employing an extraordinarily large number of flames, and consequently meeting with great difficulties in effecting an even distribution of the current.

The great importance attaching to the possibility of fixation of atmospheric nitrogen, had, several years before that time, been recognized in the Badische Anilin- u. Soda-Fabrik, and after the task of manufacturing indigo on a commercial scale had been brought to a successful conclusion in 1897, special attention was paid to this new problem, at the instigation of their head director, Heinrich von Brunck. As the result of these labors, Otto Schönherr succeeded, in 1905, in discovering, and with the assistance of the engineer Hessberger, working out a process of producing an electric arc, and was thus enabled to solve the problem in a surprisingly simple manner, presenting considerable advantages over the method of Birkeland and Eyde. It is not a mere modification of their process, as has sometimes been falsely assumed, but differs fundamentally from it, for while Birkeland and Eyde cause the electric discharge to burn in a strong magnetic field, and thus spread it out in the shape of a flat, more or less circular, disc, Schönherr dispenses entirely with magnets and magnetic fields, and produces his arc inside an iron tube of comparatively small diameter, at the same time passing the air through the tube, and thus bringing it into contact with the arc. He has described his process at a lecture in Berlin, of which a full report has just appeared in the *Electro-technische Zeitschrift* for 1909, Vols. 16 and 17. The manner in which the arc is developed is in itself very peculiar and interesting. The iron tube, or arc tube as I will designate it, contains an insulated electrode at one end, and can itself serve as the second electrode. The arc, at its formation, springs from the insulated electrode to an adjacent part of the arc tube which is only a few millimeters away, but the air, which is passing through the tube, being preferably introduced with a tangential or rotary motion, immediately carries the end of the arc along the wall of the tube, so that it either enters the tube at a considerable distance from the electrode, or it ends on a special electrode placed for the purpose, say, at the other end of the arc tube. A slight modification consists in using an arc tube of non-conducting material, and inserting in it a wire-spiral along which the end of the arc can travel, or providing other means for bringing about the initial formation of the arc. In each case, a column of flame is obtained, burning quietly in the axis of the tube, and surrounded by the air which is being passed through the tube. The arc, as seen through a mica-covered opening, emits an intense light, and is quite stable, as opposed to arcs which are formed in the open air, since these latter are easily extinguishable. The air passing through the tube comes into contact with the arc, becomes partially converted into nitric oxide, and is then rapidly cooled down by contact with the outside layers of air, and consequently a decomposition back again to nitrogen and oxygen is avoided. The cooling action is still further increased by surrounding the upper end of the arc tube with running water, after the manner of the Liebig condenser. The gases leaving the tube contain about 2 per cent. of nitric oxide, that is, from one and a half times to nearly twice as concentrated as the gases which Birkeland and Eyde produce.

The method of introducing the air can be subjected to many variations. For instance, instead of the air being passed in its entirety into the space between the electrode and the wall of the tube as shown here, it can be introduced partly or wholly into the tube at other points above or below the electrode, and it can be made to enter the tube either through one or more openings or through a number of openings which are distributed over a part or the whole of the tube. The opening may be in the form of a ring extending all round the tube, or several such ring-shaped openings can be employed, or instead of these, long slits, either parallel or at an angle to the axis of the tube, can be provided. The openings may be situated so that the air enters at right angles or at any other angle to the axis of the tube. In the latter case, the gases generally pass through the tube with a rotary motion.

With the aid of Schönherr's invention, it is possible to send extraordinarily large quantities of electrical energy through a single tube; even the small experimental apparatus which you see before you uses about 5.5 h. p. of electrical energy, and works with a tension of 5,000 volts. The experimental furnaces at Christianssand are fed with about 600 h. p. at 4,200 volts, and although it appears possible to build furnaces which could consume 2,000 h. p., those regularly used will probably be built for 1,000 h. p. These furnaces require about 40,000 cu. ft. of air every hour, and the arcs produced are nearly eight yards long.

You will probably have noticed that this process departs from the principle, hitherto followed, of bringing the air only for as short a time as possible into contact with the electric flame, for, as is evident, the air requires a not inconsiderable space of time to travel from the one end of the arc tube to the other.

The slide now shown illustrates a construction of the furnace on the large scale. The air passes into the arc tube through a number of tangentially-bored holes in the part of the tube surrounding the electrode, and over these holes is an iron ring or cylinder, which can be moved from the outside by means of a lever, so that any desired number of the holes can be closed, and consequently, the strength of the rotary motion of the air regulated, and this in turn assists in regulating the length of the arc. The insulated electrode can be cooled by means of water or air, and it is also provided with a central hollow space through which passes an iron rod. The arc actually springs from this iron rod, and as it burns or volatilizes away, it can be pushed forward by a simple arrangement; the rate of burning, however, is very slow. An ignition lever, or other simple arrangement, is provided so that the arc can be started afresh; should it from any cause become extinguished, this, however, is very rarely the case. The furnace itself is connected electrically to earth, so that any part of the apparatus, with the exception of the insulated electrode, can be handled with impunity. The gases which leave the arc tube pass down a channel lined with brick, and concentrically surrounding the inner parts of the furnace. They are thus made to give up a portion of their heat to the air which is entering the furnace, and which is subsequently passed through the arc tube, thereby raising it to a fairly high temperature.

As you see, the apparatus is extremely simple, and at the same time very durable; ordinary iron tubes are employed; there are no movable parts and no expensive electro-

magnets, and the manufacture runs smoothly without interruptions.

Though in this process there is very little loss of electrical energy in producing the arc, yet only a few per cent. of the energy serve to bring about chemical reaction; the rest is converted into heat. This latter, however, is not by any means wasted, 30 per cent. of it is employed producing hot water, 40 per cent. heats the boilers, 10 per cent. has to be removed by cooling, and only 17 per cent. is lost by radiation. The evaporation of the calcium nitrate solutions obtained is carried out solely by the heat generated in the arc.

Interesting results have been obtained by studying the chemical activity of this kind of arc. Brode showed that the inner zone of the arc was the hottest part, and in it, the formation of the nitric oxide was effected, while the decomposition back again into nitrogen and oxygen took place in the outer zone. Following up this line, Grau and Russ proposed to draw off the reaction gases from the hottest zone through very narrow cooled tubes. Haber and König found that, at a low pressure, say one-eighth of an atmosphere, and on using a tube of such diameter, that it was filled by the electric arc, and, at the same time cooling the tube from the outside, they could obtain a gas mixture with 10 per cent. of nitric oxide. The arc produced possesses a comparatively low temperature, and the experimentists believe that the combination is brought about, at any rate to a certain extent, by some electrical phenomenon, such as ionic impulses. The process is certainly very interesting from a theoretical point of view, but it is too early to give an opinion on its practical utility.

In accordance with the theory, the yield of nitric oxide increases if, instead of atmospheric air, a mixture thereof with oxygen, up to equal volumes of nitrogen and oxygen, be employed. Haber and König were able, in this manner, to obtain gases with 14 per cent. of nitric oxide. The advantages, however, are only apparent, since the production of the oxygen required is comparatively costly, and also because a very large proportion of the gases pass through the system unchanged, and are subsequently lost. The various suggestions of enriching the gases coming from the absorbers with fresh nitrogen and oxygen in combining proportions, and then feeding them into the arc tube again, and also that put forward on the one hand by Siemens & Halske, and on the other hand by Sir William Ramsay, of separating the air into its constituents, and using the nitrogen in the production of nitrolime, and the oxygen in the manufacture of air-saltpetre, do not at present appear likely to be successful.

It is interesting to note, in passing, that the arcs produced by Schönherr's process send out electrical waves, and, founded on this observation, a method has been worked out and patented by the Badische Anilin- u. Soda-Fabrik, for producing electrical oscillations of great frequency and regularity, suitable for use in wireless telegraphy.

Another process of producing electrical discharges for the purpose of obtaining nitric acid from the air has recently been described by Dr. Franz Russ at a meeting of the Society of Austrian chemists at Vienna. This is the process worked out by Pauling and utilized near Innsbruck by the Salpetersäure-Industrie-Gesellschaft of Gelsenkirchen. It depends on the use of divergent electrodes. From the data given by the author the process is inferior to the Badische process.

After the nitrogen has been converted into nitric oxide, according to any of the processes I have referred to, the actual "combustion" of the nitrogen is completed, but on cooling the reaction gases, as soon as the temperature reaches a certain point lying at about 600° C., the nitric oxide begins to combine with the excess of oxygen, forming nitrogen tetroxide. The oxidation does not go past this stage of its own accord.

The next task is to bring these oxides of nitrogen into a marketable state, that is, either into the form of nitric acid, nitrates, or nitrites; also nitrogen tetroxide as such will be capable of isolation.

Up to the present time both nitric acid and nitrites have been manufactured from saltpetre by chemical reaction, nitric acid, which is largely used in making explosives of various kinds, as well as celluloid, artificial silk, and coal tar dyes, being produced by heating saltpetre with concentrated sulphuric acid, while nitrites, also of great importance in the coal tar dye industry, result on heating sodium nitrate with metallic lead, which extracts one atom of oxygen, and is itself converted into lead oxide. Both nitric acid and nitrites are consequently more expensive than saltpetre. Nitrogen in concentrated nitric acid is two and a half times, and that in nitrites is one and a half times as valuable as nitrate-nitrogen.

It would, therefore, be more profitable to make nitric acid and nitrites, provided the consumption of these compounds were sufficiently great, but since the demand is limited, the chief aim of every large factory is to convert the supply of nitrogen into the form of saltpetre, for which, as we have seen, there is an unlimited market. Before the nitrogen tetroxide contained in the furnace gases, after they have been cooled, is capable of yielding nitric acid, it requires to be combined with a further atom of oxygen, and this combination is generally brought about by the action of water. The gases are passed through an absorption tower down which water is trickling, and during the reaction which takes place, two-thirds of the nitrogen is converted into nitric acid, while one-third is regenerated as nitric oxide, which combines again with the excess of oxygen present in the gases forming nitrogen tetroxide, and this goes through the same course of reactions again. This constitutes the so-called "acid" absorption process. The absorbing liquid can be run down the tower several times, each time becoming richer in nitric acid, until a 40 per cent. acid is obtained. On neutralizing this with soda, a concentrated solution of sodium nitrate is obtained, and can be evaporated until the solid salt crystallizes out. On a practical scale, however, ordinary limestone is employed instead of soda, and calcium nitrate is obtained. This is at least as valuable as sodium nitrate for manuring purposes, and is consequently isolated as such, and brought on the market under the name of "Norwegian saltpetre" or "air-saltpetre."

If it be desired to obtain marketable nitric acid, the 40 per cent. acid obtained by absorption must be concentrated, and there are several methods available for this purpose. Most of them depend on the removal of water by means of sulphuric acid or certain anhydrous salts, and another process has been proposed, in which the water is removed indirectly by means of electrolysis.

Nitrites can be obtained directly from the furnace gases, by employing sodium carbonate or milk of lime as the absorbing agent, and at the same time maintaining the temperature and other conditions, such that, during the absorption, the gases contain equal quantities of nitrogen tetroxide and unaltered nitric oxide. According to this process, the Badische Anilin- u. Soda-Fabrik manufacture, at Christianssand, the sodium nitrite they require in their dye factory at Ludwigshafen.

Finally, if the reaction gases be cooled down to a temperature considerably below zero, nitrogen tetroxide separates out as a liquid, or, if the temperature be sufficiently low, it can even be obtained in the solid state, like ice or snow. Should the gases contain moisture, more or less dilute nitric acid is produced, the quantity depending on the amount of water present.

A further method of working up the furnace gases consists in passing them over quicklime. Halvorsen carried out this process at ordinary temperature, while Schloesing obtained better results by working at a raised temperature. The latter employs special briquettes of quicklime, prepared by moulding slaked lime into the required shape, and then reheating it, and he places these briquettes in iron vessels, and heats them on the counter current principle, by means of the furnace gases, to from 300–350° C. The final product of absorption contains dry calcium nitrate in admixture with free lime, and some calcium nitrite.

The absorption at Notodden is at present carried out according to the "acid" process; the first product is dilute nitric acid, which is subsequently converted into calcium nitrate. The apparatus necessary is very extensive, on account, both of the small contents of nitric oxide in the gases, and also of the very large volume of the gases treated. The hot gases, on leaving the electric furnace, are first made to pass through boilers, thereby giving up some of their heat, and creating the supply of steam used for heating the vacuum pans, in which the solutions of calcium nitrate are evaporated. These vacuum pans can be heated directly by the furnace gases if desired, or by the intermediate agency of steam. The gases are then still further cooled and afterwards passed into a large empty tower or other receiver, in which time and opportunity are given for the nitric oxide to be oxidized to nitrogen tetroxide. If the gases contain 2 per cent. of nitric oxide, 12 seconds are required for the oxidation of 50 per cent. of it, while the oxidation of 90 per cent. requires 100 seconds. The gases are then passed into very large granite towers about 65 ft. high, and filled with lumps of quartz, and, in these towers, the acid absorption is effected by means of water, or of the dilute nitric acid which is collected at the bottom of the tower. In order to recover the oxides of nitrogen which remain unabsorbed, the gases are finally treated with milk of lime or soda, and give rise either to a mixture of nitrite and nitrate, or to pure nitrite.

The more dilute the gases are, the more difficult is the absorption, and consequently the greater concentration of the gases obtained by the process of the Badische Anilin- u. Soda-Fabrik constitutes a not unimportant advantage over Birkeland and Eyde's process.

More recent experiments at the Badische Anilin- u. Soda-Fabrik have shown the possibility of effecting the absorption directly with milk of lime, and, in this case, the "acid" absorption could be dispensed with, and the absorbing towers and the initial outlay on plant considerably reduced

The calcium nitrate, obtained by means of the operations described, can, without further treatment, replace Chili saltpetre for the purposes of agriculture. Even a certain quantity of free lime, say 20 per cent., appears to have no deleterious action on vegetable life, and the same remark applies to any calcium nitrite mixed with the nitrate. In fact, experiments carried out by Wagner at Darmstadt last summer, corroborate the results obtained by Schloesing and show that no difference can be noticed between the crops obtained, whether the soil be treated with Chili saltpetre, or with pure calcium nitrate, or with a mixture of this latter with 10–20 per cent. of calcium nitrite, or even with pure calcium nitrite. It is by no means inconceivable, that calcium nitrite will become the artificial manure of the future, especially as its manufacture is so simple, and it is richer in nitrogen than calcium nitrate (it contains 21.2 per cent. of nitrogen). It possesses the further advantage of being less hygroscopic than calcium nitrate.

Both the process of the Badische Anilin- u. Soda-Fabrik and of Birkeland and Eyde require cheap water power, before they can be carried out profitably. The waterfalls in Norway, which, owing to the climate, have a fairly constant supply throughout the year, are particularly suitable. The Badische Anilin- u. Soda-Fabrik secured the right of using several falls there, and commenced by putting down an experimental plant at Fiskaa near Christianssand. A few thousand h. p. were available, and manufacture was started in the autumn of 1907.

In the meantime the Norsk Hydro Elektrisk Kvaelstof-Aktieselskab, that is, the Norwegian-French Company founded by Birkeland and Eyde, had commenced building a factory at Notodden to use up 30,000 h. p. The interests of the two companies lay in the same direction, and negotiations were opened, and, towards the end of 1906, resulted in an agreement, according to which the Badische Anilin- u. Soda-Fabrik and its two allied firms, the Farbenfabriken vorm. Friedr. Bayer & Co. of Elberfeld and the Actiengesellschaft für Anilinfabrikation in Berlin on the one side, and the Norwegian-French concern on the other side, combined forces and floated two new Norwegian companies. These were:

(1) A power company with a capital of 16,000,000 Kronen, whose duty it is to develop and bring into harness further Norwegian waterfalls, and

(2) The Norsk Salpeterverker with a capital of 18,000,000 Kronen, which is concerned in building and running Norwegian saltpetre factories, making use of the power supplied by the first company.

The two parties have come to an arrangement as to the exploitation of their patents outside Norway, and the granting of licenses lies in the hands of the Badische Anilin- u. Soda-Fabrik. The works at Christianssand and Notodden remain the special property of the original owners.

The first large factory erected by the new Norwegian companies will be situated in the interior of Telemarken on the Rjukan, one of those immense waterfalls in Norway. The total fall of 1820 ft. is divided into two steps, and, with a flow of about eleven thousand gallons of water per second, is capable of yielding a quarter of a million horse-power. The upper fall is now being developed, and with ten turbines

will provide about 140,000 h. p. It is expected that the factory will start running in about two years' time. The saltpetre will be carried along 29 miles of new normal-gauged railway, and by a ferry along Lake Tin, which is 25 miles in length, until it reaches Notodden, from here it will be transported *via* Skien to the sea. At present, the Norsk Hydro Kvaelstof-Aktieselskab is using up 30,000 h. p. at its factory at Notodden, where 35 of Birkeland's furnaces have been erected, and, at the present time, an experimental plant on the system of the Badische Anilin- u. Soda-Fabrik is being constructed there, in order to determine which type and size of furnace is most suitable for erection at Rjukan. Water power on the Matre and on the Tyn in West Norway have been acquired, and will be held in reserve for future use.

In Germany, the water power suitable for the production of saltpetre is very limited. In South Bavaria, the Alz is able to supply sufficient power for a moderately large factory, and negotiations have already taken place with the Bavarian Government, with regard to a scheme for the production of 50,000 h. p., and the erection of a factory near Burghausen. Negotiations have also been going on for some time with a view to the introduction of the manufacture into this country, but here also suitable water power is hard to find.

Considerable quantities of air-saltpetre will shortly be put on the market, and probably, within a few years, the annual output will reach 100,000 tons. This quantity, however, is none too large, when we remember that the world's demand increases by at least that much every two years, and we need not expect any demoralization of the saltpetre market. On the other hand, it is not likely that Chili saltpetre will unfavorably influence the development of the factories already started, especially as air-saltpetre has decided advantages over Chili saltpetre, since it is free from injurious admixtures of perchlorate and other compounds, which are contained in the natural saltpetre; then again air-saltpetre is able to supply the lime, which is indispensable if the plant is to flourish, whereas the soda of Chili saltpetre is very often directly harmful. Experiments have been made at Grandeau, Sjolemma, and others, showing the great advantage of using air-saltpetre on soils which are poor in lime.

It has recently been asserted by Caro, that it is more rational to manufacture nitrolime than air-saltpetre, because the former requires only one-third of the amount of electricity to fix the same quantity of nitrogen, and the economy of both processes depends on the quantity of power used. Such a comparison can easily lead to confusion. The production of air-saltpetre requires, in addition to electrical power, only the very cheapest materials, namely water and limestone, whereas, in order to produce nitrolime, coal has to be employed, and, in addition, the nitrogen used in the process cannot be taken in the form of air, but first must be separated from the oxygen. These points have to be taken into consideration; it is not sufficient merely to compare the electrical energy used in each case. Moreover, there are other points in favor of the production of air-saltpetre. Not only has the nitrogen contained in it a higher value than that in ammonium sulphate, or in nitrolime, but, by the oxidation of nitrogen, the nitric acid, nitrates and nitrites which are so indispensable in the chemical industry are obtained. These compounds have a higher value than air-saltpetre, the nitrogen in nitric acid being worth more than twice as much as that in ammonia. The prospects of a profitable conversion into nitric acid, of the ammonia obtained from nitrolime, appear very doubtful.

As a matter of fact, however, our previous considerations have shown us that the world's demand for combined nitrogen is growing so enormously, that there is room and to spare for these two processes and others as well to develop side by side.

It has in recent times been suggested that the large waterfalls in Germany should be taken over by the State, for the purpose of electrifying the railways, for lighting purposes, and for supplying power to small manufacturers. It is, however, difficult to find a purpose to which the waterpower could be better applied in the interests of the State, than in the production of combined nitrogen, and further, there is, at the present time, no other industry which would be in a position to take up such large quantities of cheap power. We have a classical illustration of this in the case of Norway, where, although small quantities of water power are sought after, up to the present, it has been difficult to find a use for the large waterfalls. This is probably due to the fact, that the distribution of electricity, in those parts of the country in which the population is scattered, and the houses and small villages lie far apart, would require so high an outlay for installation, that a general adaptation for lighting purposes, and for supplying power on a small scale, is out of the question. The reverse, however, applies to the utilization of the large falls for the production of air-saltpetre; such production would be coupled with remarkable advantages, for it would open up large industries, just in those parts of the country which from natural causes have hitherto been most neglected. Another factor which must not be underestimated when considering the advantages of the new air-saltpetre industry, is its non-participation in the destruction of the valuable coal deposits, which have been stored up for us during such countless ages. It obtains the power it requires from water, or as it has been fancifully termed "white coal," which can be employed over and over again without being exhausted, since as soon as it has been used, it is raised up again into the sky by the agency of the sun, and this circulation has gone on through countless ages, and will continue as long as we have any need of saltpetre.

We have consequently every reason, from such different points of view as those of the agriculturist, the industrial chemist, and the whole of mankind, to hope that the new process for the combustion of nitrogen will continue to develop and flourish.

NOTES AND CORRESPONDENCE.

A USEFUL FORM OF PYCNOMETER FOR DETERMINING THE SPECIFIC GRAVITY OF SEMI-SOLID BITUMENS.

The inconvenience and difficulty of employing the ordinary narrow-neck pycnometer when determining the specific gravity of dense residual oils and soft tar pitches has led the writer to devise a modified form suitable for use in this connection. A description of this apparatus is therefore given for the benefit of those who have occasion to determine the specific gravity of such materials. Except in cases

where extreme accuracy is desired, this pycnometer is also suited for determinations of non-volatile oils, especially those of too high viscosity for use with the Westphal balance or hydrometer.

The pycnometer, as shown in Fig. 1, consists of a fairly heavy, straight-walled glass tube, 70 mm. long and 22 mm. diameter ground to receive a solid glass stopper with a 1.6 mm. bore in place of the usual capillary opening. The lower part of this stopper is made concave in order to allow all air bubbles to escape through the bore. The depth of the cup-shaped depression is 4.8 mm. at the center. The stoppered tube has a capacity of about 24 cc. and when empty weighs about 28 grams. Its principal advantages are that (1) any desired amount of bitumen may be poured in without touching the sides above the level desired; (2) it is easily cleaned; (3) on account of the 1/16″ bore the stopper can be more easily inserted when the tube is filled with a very viscous oil, than if it contained a capillary opening.

When working with semi-solid bitumens which are too soft to break and handle in fragments, the following method of determining their specific gravity has been employed by the writer with good results. The clean, dry pycnometer is first weighed empty and this weight called "*a*". It is then filled with freshly distilled water at 25° C. in the usual manner, the weight again taken and called "*b*." The bitumen should be brought to a fluid condition by the gentle application of heat, care being taken that no loss by evaporation occurs. When sufficiently fluid enough is poured into the pycnometer to about half fill it, without allowing the

FIG. 1

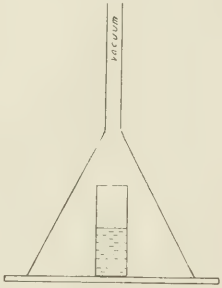


FIG. 2

material to touch the sides of the tube above the desired level. If the presence of air bubbles is suspected, the tube may then be placed for a few minutes in a vacuum chamber made by inverting a large glass funnel on a ground-glass plate, as shown in Fig. 2, the edge of the funnel being smeared with desiccator grease. After all air bubbles have thus been removed, the tube and contents are cooled to 25° C. in any suitable manner and weighed with the stopper. This weight is called "*c*." Distilled water at 25° C. is then poured in until the pycnometer is full, the stopper inserted and the whole weighed. This weight is called "*d*." From the weights obtained, the specific gravity of the bitumen may be readily calculated from the following formula:

Specific gravity, 25° C./25° C. = $c - a/(b-a) - (d-c)$

Check results obtained according to the above method are accurate to within two units in the third decimal place as compared with the open-tube method commonly employed which is accurate to the second decimal place only.

The specific gravity of fluid bitumens may be determined in the ordinary manner with this pycnometer by completely filling it with the material and dividing the weight of the bitumen thus obtained by that of the same volume of water.

The pycnometer may be readily cleaned by placing it in a hot-air bath until the bitumen is sufficiently fluid to pour. As much is drained out as possible and the interior swabbed with a piece of cotton waste. It is then rinsed clean with a little carbon bisulphide. PREVOST HUBBARD.

LABORATORY, OFFICE OF PUBLIC ROADS,
U. S. DEPARTMENT OF AGRICULTURE.

THE DETERMINATION ON ZINC BY WEIGHING AS SULPHATE.

This method is similar to the determination of cadmium, manganese, cobalt, magnesium and calcium as sulphate. It has been in use by one of the writers for some years and has given perfectly satisfactory results. The zinc is precipitated customarily as sulphide from a hot solution slightly acid with sulphuric or hydrochloric acid, to which ammonia is added during precipitation until the solution is but faintly acid. Precipitation made in this way is complete and the precipitate is readily filtered and requires washing with hot water only.[1] As will be shown presently, removal of all traces of ammonium salts is not necessary. The zinc sulphide is washed into a deep beaker with as little water as possible and dissolved in hydrochloric acid which has trickled through the filter paper in order to take up any sulphide still adhering. To avoid effervescence during subsequent evaporation the solution in the covered beaker is boiled until hydrogen sulphide is completely expelled; it is then transferred to a weighed porcelain crucible and evaporated on the water bath after addition of only a little more than the quantity of sulphuric acid necessary to form zinc sulphate. When no further evaporation takes place, the crucible is placed in a small air bath, either a Hillebrand radiator[2] or a large porcelain crucible fitted with asbestos ring as described by Treadwell.[3] The excess of sulphuric acid having been removed by heating in such an air bath, the crucible is cautiously subjected to the direct heat of the Bunsen flame and finally heated to redness for several minutes. The crucible with zinc sulphate is colored in the desiccator and weighed.

The results are as a rule accurate to within one or two-tenths of one per cent.

A solution of zinc chloride was made by dissolving J. T. Baker's chemically pure "analyzed" zinc in hydrochloric acid and diluting so that 50 cc. of solution contained 0.3005 gram zinc. In measured volumes of this solution the zinc

[1] See Waring, "On Precipitation from Formic Acid Solution," *Jour. Am. Chem. Soc.*, **26**, 27 (1904).

[2] *Bulletin* **305**, *United States Geological Survey*, page 29.

[3] "Quantitative Analyse," fourth edition, page 24.

was determined as sulphate and, for comparison, as pyrophosphate by the method given by Waring.[1]

In these determinations the solution for analysis was measured out by one of the writers and the determination made by the other, so that the analyst had no knowledge of the result which he was expected to get.

TABLE I.

DETERMINATION OF ZINC AS SULPHATE AND PYROPHOSPHATE, WITH CALCULATED RESULTS.

Found.	Calculated.
As sulphate	
0.3043 g. zinc.	0.3035 g. zinc.
0.1541	0.1533
0.0909	0.0909
0.2428	0.2425
As pyrophosphate.	
0.2861 g. zinc.	0.2854 g. zinc.
0.1656	0.1656
0.2224	0.2223

To determine whether or not the presence of small quantities of ammonium chloride affects the result, either by remaining unvolatilized as sulphate or by causing volatilization of zinc chloride, zinc chloride solutions were evaporated with sulphuric acid and a few milligrams of ammonium chloride. The outcome of these experiments (Table II) makes it clear that for this determination it is not necessary to wash precipitated zinc sulphide perfectly free from ammonium chloride which may contaminate it. It should be added, however, that larger quantities of ammonium chloride (100 mg. and over) cause low results.

TABLE II.

INFLUENCE OF AMMONIUM CHLORIDE ON DETERMINATION OF ZINC AS SULPHATE.

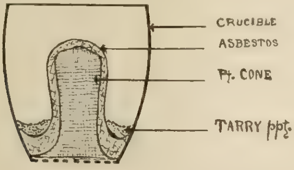
Found.	Calculated.
0.1803 g. zinc.	0.1803 g. zinc.
0.1804	0.1804

EUGENE C. SULLIVAN,
W. C. TAYLOR.

CORNING GLASS WORKS,
CORNING, N. Y.

THE PREPARATION OF GOOCH CRUCIBLES FOR ASPHALT ANALYSIS.

The filtration of tarry or asphaltic precipitates suspended in organic solvents on porcelain Gooch crucibles is a tedious and unsatisfactory process at best. The following simple deviation from the ordinary method of preparing such crucibles has proven itself of value in several hundred determinations carried out in this laboratory.



A thimble-shaped cone of platinum gauze is placed in the bottom of a Gooch crucible and the asbestos sucked dry over it as shown in the accompanying cut. In cases where it is not necessary to ignite the precipitate, fine copper gauze has proven itself satisfactory. In use, the cone not only furnishes increased surface for filtering but also allows the denser part of the precipitate to settle in a ring at the bottom of the crucible, leaving the asbestos on the apex of the filter in such a condition that the filtrate and washing liquids can be quickly and completely removed.

B. MEARS.

UNIVERSITY OF ILLINOIS,
MAY 31, 1909.

[1] *Jour. of the Amer. Chem. Soc.*, **26**, 28 (1904).

THE DETERMINATION OF OXIDES OF IRON AND ALUMINA IN FLORIDA PHOSPHATES.

The method as given below is a modification of the old Glaser method, and can be depended upon to give excellent results in all except the few instances in which manganese occurs in any appreciable quantity. It must also be noted that this method does not include any iron or alumina present in the shape of pyrite, or as a silicate insoluble in acid. With reasonable care in the various operations, the results on the identical pulverized sample should not differ more than 0.05 per cent. and are generally well within this limit. The most important points appear to be the proper elimination of fluorine, and the use of *very hot* water in washing the precipitate. As carried out in this laboratory, the operations are as follows:

One gram of the powdered sample is carefully weighed out and placed in a tall beaker of about 300 cc. capacity Ten cc. of strong muriatic acid are added, and after covering with a watch glass, the beaker is placed on a gauze and quickly brought to a boil. Leave on the gauze for ten minutes, regulating the flame so that it does not go dry, and the bulk of the solution at the end of the ten minutes is about 5–7 cc. Let cool, and carefully decant as completely as possible into a Jena glass volumetric flask of 100 cc. capacity. Try to get all the solution to run into the flask, excepting the last drop or so. Rinse this last drop into the flask with the least possible amount of water. It is possible to do this with a little practice, without disturbing the bulk of the sand, which remains (most of it) in the original beaker. You now have about 10–12 cc. solution in the little volumetric flask. To this solution in the flask you add 10 cc. of dilute sulphuric acid (one-half acid of 1.84 sp. gr., and half water).

The addition of this acid will form a curdy, bulky precipitate of impure sulphate of lime. Shake up the flask to mix this precipitate, and then place the flask on a gauze over Bunsen in the hood, and boil for at least ten minutes.

It may require a little practice to get the flame just right, to get the flask and contents to boil hard without bumping off the stand but it is most important that the contents should boil. This boiling gets rid of nearly all the fluorine, and changes the bulky precipitate of calcium sulphate into a dense, crystalline compound, which filters and washes easily. My experience has been that a gauze and Bunsen are better than hot plate or sand bath for this particular operation, as a quick heat gets the solution to a temperature where the violent pumping (caused by the occasional liberation of a large bubble of vapor) is avoided by causing the evolution of steam, etc., to be so rapid as to form a more continuous stream.

After ten minutes' boiling, take the flask off the fire and let cool to room temperature.

To go back to the beaker in which the original solution was made, it is possible that the grains of sand and insoluble matter might not have been rinsed quite clean in transferring to

the flask. It is therefore the practice to add to this residue a few cc. of alcohol (95 per cent.). These alcoholic rinsings are now added to the cooled flask containing the dense calcium sulphate and the solution made up to the mark with alcohol and allowed to stand at least one hour. (It will not hurt to stand over-night.)

There is some shrinkage in this alcoholic solution, which must be made up to the mark with more alcohol.

After standing, the solution is filtered on a dry filter into a dry beaker, or into a dry porcelain evaporating dish of about 5 inches diameter, if all the solution is to be used.

In case the flask is graduated to allow for the bulk occupied by the calcium sulphate precipitate, the dry beaker is used to catch the filtrate—and an aliquot portion of 75 cc. is withdrawn with a pipette and this aliquot (corresponding to 3/4 gram) is used for the further tests. If you have not allowed for the bulk of the precipitate, it will be necessary to filter *all* the solution from the flask, and wash it with alcohol until free from foreign matter.

Assuming that you have withdrawn 75 cc. for analysis, place this in the 5-inch evaporating dish, and then place the dish in a pan containing about one-half inch in depth of water. This water is used simply for cooling purposes, and must not be too deep, or your dish will be liable to crack. Now add about 5 cc. of bromine water to your alcoholic solution, pouring it down the side of the dish carefully, so it will run under the alcoholic solution, without mixing any more than can be helped. Then simply light the alcoholic solution with a match. The alcohol will burn off in from 10–15 minutes. The water outside prevents the solution from getting too hot, and spattering.

When the solution has burnt out and cooled, add 10 cc. concentrated solution of ammonium chloride. A few drops of rosolic acid solution as indicator are now added, and ammonia water till distinctly red.

The dish is transferred to the water bath, and heated until the red color is changed to a yellow. A little hot water is used to mix and dissolve any crusts that may have formed. Use water as hot as possible, and just before putting on the filter, add ammonia very cautiously till it is faintly pink, and mix well by squirting in a fine stream from your wash bottle. Then throw on a good tight 12½ cm. filter (either S & S 589 or Munktell's 00) and let it all run through before adding the rinsings from the evaporating dish. The washing should be done without disturbing the layer of precipitate on the filter, and the water used should be as nearly boiling as possible. Usually (unless the percentage is very high), about three to four washings are sufficient to remove all the foreign matter.

The moist precipitate on the filter is now placed in a 20 cc. platinum crucible and dried over a very low flame. Then it is charred at a low red (don't let it catch fire) and finally ignited over a good Bunsen.

The weight of this precipitate is equivalent to the weight of the phosphate of iron plus phosphate of alumina. In most of the older contracts, one-half of this weight was the figures referred to when speaking of oxides of iron and aluminum, "combined."

It must be remembered, that in case only 75 cc. were operated on, that correction should be made to figure proper percentages from 3/4 to 1 gram. This matter of taking one half the weight of the phosphates to be the oxides of iron and alumina, "combined," has been sanctioned by custom, but is manifestly incorrect. It is therefore necessary to separate at least the iron in order to get at the actual percentages.

To do this, the ignited oxides in the platinum crucible, are dissolved in dilute sulphuric acid on the hot plate. The solution takes place easily, leaving only a skeleton of filter ash.

This solution can be made up to 100 cc. and the iron titrated in say 50 cc. with permanganate, and in the other 50 cc. the phosphoric acid, or the alumina, may be determined. Then it is a simple matter of calculation to get at the actual percentages of iron and alumina in the sample under examination.

H. Herzog.

LEAD NUMBER OF VANILLA EXTRACTS.

In a study of vanilla extracts made in this laboratory, from the different varieties of vanilla beans, it was suggested by one of the authors that the Winton[1] lead number might prove of value in establishing the purity of an extract. Accordingly, the following determinations were made.

The extracts were all made from 10 grams of beans to each 100 cc. of extract by a method of very slow percolation which we believe attains practically complete extraction.

Table I.

Lead numbers.

Bean.	Experiment.	Per cent. alcohol.	Lead number.	Duplicate.	Per cent. dry matter in beans used.
Prime:					
Mexican..........	2	65	1.62		
Mexican:					
Cuts.............	4	50	1.82		
"	5	50	1.91		
"	6	50	1.90		
Prime:					
Mexican..........	8	65	1.60		
"	9	20	1.64	1.63	67.14
"	10	30	1.68	1.68	67.14
"	11	40	1.66	1.65	67.14
"	12	65	1.65	1.65	67.14
Ordinary:					
Mexican..........	13	20	1.80	1.82	82.63
"	14	30	1.82	1.80	82.63
"	15	40	1.81	1.81	82.63
"	16	65	1.83	1.80	82.63
Mexican:					
Cuts.............	17	20	2.00	2.00	80.18
"	18	30	2.03	2.01	80.18
"	19	40	2.10	2.09	80.18
Bourbon	21	20	1.56	1.55	
"	22	30	1.59	1.59	62.64
"	23	40	1.68	1.68	
"	24	65	1.60	1.60	
South American...	25	20	1.62	1.62	
" " ...	26	30	1.42	1.42	82.36
" " ...	27	40	1.48	1.47	
" " ...	28	65	1.51	1.49	
Vanillons	29	20	1.02	1.02	92.21

It was then noticed that the "Lead Number" was practically a constant for any particular bean regardless of the per cent. of alcohol used in the percolation, which would indicate that practically all of the bodies precipitated by

[1] *Jour. Am. Chem. Soc.*, **28**, 1204.

basic lead acetate were removed by any strength of alcohol likely to be used, and that the "Lead Numbers" could be used as a measure of the quantity of vanilla beans used in the manufacture of an extract.

To test this point three extracts were made up as before, but with 5, 10, and 15 grams of beans to each 100 cc. The results follow:

TABLE II.

Lead numbers.

Bean.	Experiment.	Per cent. alcohol.	Lead number.	Duplicate.	Grams in 100 cc.
Bourbon	A	65	0.84	0.83	5
"	B	65	1.68	1.68	10
"	C	65	1.79	1.80	15

Experiments A, B, and C seem to indicate that the "Lead Number" is a measure of the quantity of beans used when this does not exceed 10 grams in 100 cc. The work had to be brought to a close at this point, but will be taken up again shortly and a more extended study of this point will be made.

It was thought that the data presented was significant enough to warrant its publication.

H. LOUIS JACKSON,
WM. T. MCGEORGE, JR.
CONTRIBUTION FROM THE FOOD LABORATORY,
KANSAS STATE UNIVERSITY.

THE MEASUREMENT OF CRUDE SULPHURIC ACID.

There are many difficulties encountered in actually weighing and determining the amount of chemically pure sulphuric acid in acid at fertilizer plants. Because of this fact most of the figures expressing quantities of the crude acid are obtained by calculation from the volume of the acid and the specific gravity or equivalent Baumé.

Temperature is an important item in these calculations which is sometimes ignored and at other times incompletely or incorrectly taken into consideration.

A case of the latter which affects both the yield of the acid plant and the formula used in acid phosphate manufacture is sometimes found where the measured acid used in the acid phosphate department.

The volume of acid and Baumé are taken at a high temperature. The equivalent Baumé at 60° F. is calculated and used in looking up in the sulphuric acid table the compounds per cubic foot of acid in the volume measured, thus erroneously supposing that if the acid had cooled down to 60° F. it would still occupy the same volume that it did at the high temperature.

The following example will illustrate this point:

Given 1 cubic foot of acid measured at 120° F. and reading 51 Bé. Required the equivalent weight of 50 acid at 60° F.

51 acid at 120° is equal to 52.68 acid at 60°.

Erroneous Method.—From the table[1] we find 1 cubic foot of 52.58 Bé. acid at 60–1042 lbs.

Correct Method.—51 acid according to the same table weighs 96.21 lbs. per cubic foot, and this weight remains constant when the acid is cooled to or reduced 52.68 Bé. at 60. Referring again to the table we find that 52.68 Bé. acid contains 106.38 per cent. 50 acid at 60 96.2 1 x 1.0638 : 102.35 lbs. at 50 acid at 60.

Difference in the two methods 104.21 — 102.35 — 1.86 lbs. per cubic foot or an error of nearly 2 per cent. if the first method is used. The error varies directly with the temperature at which the observations are made.

Besides affecting the acid phosphate formulas, in plants where the entire output of acid is used in acid phosphate, the error given in the example above would increase an actual yield of 485 in the acid plant to the impossible figure 494.

To facilitate these correct calculations a table has been worked out based on the table referred to above, giving the number of pounds 50 Bé. acid in one cubic foot for each one-tenth degree Bé. and for each ten degrees temperature so that we are now able to easily and correctly take into account the temperature on all measurements. It may be argued that the neglect of temperature in measuring stock on hand for calculating the yield in acid works will give the same results on a year's average. It seems, however, desirable to exclude the effect of warm and cold weather on yield and make the yield from week to week as accurate as possible.

There is a commendable tendency in some plants at least to have this and similar accuracies replace the practices of some of the older acid men who in the past often held in reserve a hundred tons or more of acid and by putting this in or taking out of stock made a uniform yield no matter whether the chambers did good work or not. Greater confidence in yield and formula figures will result. The extra trouble necessary to explain to the management an occasional erratic yield will be amply repaid by this confidence.

F. B. PORTER.
CHEMICAL LABORATORY,
SWIFT FERTILIZER WORKS,
ATLANTA, GEORGIA.

[1] "Sulphuric Acid" Table approved and adopted as a standard by the Manufacturing Chemists' Association of the United States June 23rd, 1904, New York.

METHOD OF AVOIDING EMULSIONS IN ORGANIC ANALYSIS.

One of the most troublesome things the chemist has to deal with in organic analysis is the matter of the formation of emulsions between an aqueous and a non-aqueous layer of oil or solvent. There have been suggestions for breaking and avoiding emulsions in the text-books and journals and those that have impressed the author to any extent are briefly as follows:

I. Heat tends to break emulsions.

II. A little alcohol added to an ether layer more or less emulsified with an aqueous layer has a clarifying effect.

III. Filtering through a paper filter moistened with water or the solvent (generally water, as it is heavier in most cases than the organic solvent) breaks up some emulsions.

IV. Adding more solvent or more water or both.

V. Making the mixture as nearly neutral as possible.

VI. Keeping the concentration of the aqueous layer above a certain minimum as dilution below this minimum aids in causing a milky emulsion.

VII. Centrifugation.

VIII. Avoiding air bubbles and insoluble substances.

IX. Driving off water from an emulsion and extracting in a Soxhlet.

The method that the author generally resorted to in the past when stubborn emulsions were met with or known to

be inevitable, if the simple course of procedure were followed, was to evaporate to dryness in the presence of filter paper or asbestos to absorb the substances to be extracted and then to carry out the extraction with the solvent desired in a Soxhlet extractor. After saponifying lard and neatsfoot oils which were compounded with mineral oils, it was found that it expedited matters to absorb the whole mass in asbestos, drive off all water and extract with ether. This is a fairly good way to proceed but the author has recently found a simpler and quicker way. These points are mentioned to convey an idea of the trouble involved in making a separation of some mixtures of saponifiable and unsaponifiable oils. Animal oils are much more troublesome than vegetable oils. Mixtures of lard or neatsfoot oil and mineral oil, sperm oil and hide grease are examples of troublesome mixtures with which to work.

The method that has been followed in this laboratory for some time for mixtures of this kind depends upon the presence of relatively large amounts of alcohol which holds both the neutral and the saponifiable oil in solution or suspension. It has been found to give uniformly good results and is as follows:

1. Method Used when Non-saponifiable Is To Be Determined.

Saponify in a flask in the usual way with alcoholic potash or sodium or potassium alcoholate, and when the saponification is complete evaporate about half the alcohol unless the soap formed separates on cooling in which case more alcohol should be added until it dissolves. If a short glass tube is used as air condenser by the time the contents of the flask have boiled sufficiently about half the alcohol will have gone off. Add rather more than an equal volume of ether, and transfer, by washing the contents of the flask with ether into a separatory funnel. Now add water while slowly rotating the flask until after a separation of the layers no further turbidity occurs in the lower layer on adding more water. About 5 or 6 volumes of water are added in this way. Draw off the lower layer to another funnel and add more water and shake out with more ether and separate, when both layers are clear. This extract may contain a little non-saponifiable oil and is added to the main body of the ether solution of non-saponifiable oil after the first ether layer containing the bulk of the non-saponifiable oil has been washed two or three times with water to remove alcohol that was dissolved in the ether.

After washing free of soap and alcohol, this ether extract with the second ether extract is evaporated in a tared flask and weighed. We have carried out this procedure for several months on the classes of oils mentioned above and have never had one troublesome emulsion. In most all cases there was practically no waiting necessary, as the layers separated perfectly in a few minutes. It does not matter how much free alkali is present. There would obviously be some difference in the amount of dilution of the alcohol necessary with different non-saponifiable substances, such as higher alcohols or mineral oils. In the case of mineral oil as the non-saponifiable matter, the author had very little doubt on the subject, as it is only slightly soluble in strong alcohol and when the alcohol is diluted to 20 per cent. strength it apparently holds a very minute amount, as the second shaking out with ether removes it all. In the case of an oil that it was thought might contain some saponifiable matter, but was all mineral oil, 99.5 per cent was recovered after treating by this process.

In the case of higher alcohols the method seems to give as reliable results as with mineral oil although the slight solubility of the alkaline soaps from waxes may make it necessary to follow Method IX before referred to.

2. Application of the Method when Determining Free Acid in Oils.

In the determination of free acid in oils where the molecular weight is not known, it is not sufficiently accurate to titrate with caustic potash solution and calculate it, say, to oleic acid. In such instances it is necessary to neutralize and remove the free acid and to weigh up the residual neutral oil. This has been a difficult thing to accomplish however, due to emulsions in many instances. If the method given above, with slight modifications, is used there is no trouble on this score.

Dissolve the oil in ether and add an equal volume of alcohol and a few drops of phenolphthalein solution. Then add approximately normal caustic potash solution until very slightly alkaline, put in a separatory funnel rinsing the weighed beaker with about as much ether as was used in the first instance and then add water slowly until all the oil seems to be separated from the lower layer. Rotate carefully to wash most of the alcohol out of the ethereal layer and allow to settle until clear. Draw off the lower layer into a second separatory funnel, wash the ethereal layers with water and the aqueous layer with ether after adding more water. Unite the two ether layers and wash with a little more water. Evaporate the ether in a tared flask. This residue is the neutral oil and the difference between the two weights is the free acid. With the application of this method to cases I and II, other solvents such as chloroform or benzol may be employed, but ether gives much better separations.

3. Breaking Emulsions.

In general, if it is necessary to extract an ethereal solution with aqueous alkali, proceed either according to the method just described of determining free acid in oils or as follows:

If an emulsion has formed, add alcohol until a clear solution or clear layers result, then twice as much (or more) ether as alcohol is added and then slowly add water and rotate the flask or separatory funnel until no more oil separates from the aqueous layer. Sometimes this may take several hundred cubic centimeters of ether and may seem wasteful, but when the time saved is considered and the fact that the ether in both layers is recoverable that objection is removed. S. S. SADTLER.

LABORATORY OF SAMUEL P. SADTLER & SON.
PHILADELPHIA, PA.

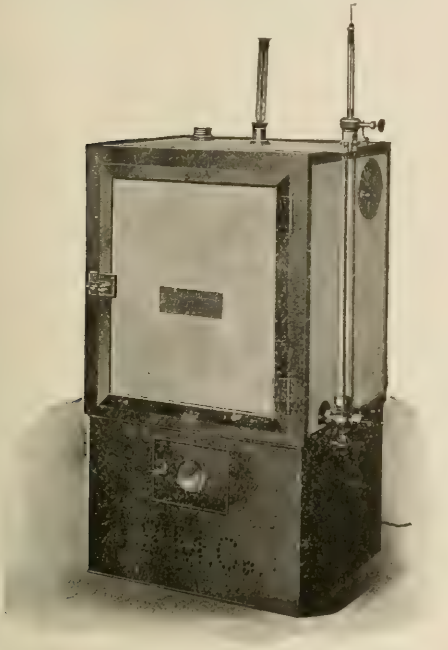
AN ELECTRICALLY HEATED INCUBATOR.

A recent improvement in laboratory apparatus, for which there was a real demand, is the electrically heated bacteriological incubator. In all probability it will, within the near future, replace the old style gas-heated incubator, and for this reason a brief description will be of interest to all who have occasion to use such an apparatus.

The difficulty of maintaining a constant temperature and the liability of fire in the gas-heated incubators are well known to those who have used them. Consequently, a simple arrangement which will overcome these will be welcomed.

The apparatus consists of a three-walled oven made of copper, providing a water jacket and an air space. The

latter continues down into the base, which contains two or more ordinary incandescent lamps, depending upon the size of the incubator. A mercury thermo-regulator is inserted in the water jacket, the bulb of which contains about two pounds of mercury and has a capillary glass tube attached, through which the expansion and contraction takes place, thus magnifying any slight change of temperature.



The current passing through the regulator is automatically closed or opened by the rise or fall of the mercury in the capillary tube, the point of contact being adjusted by turning the screw provided for this purpose.

The incandescent lamps in the base and the regulator are connected with a make and break device, which constitutes the simple arrangement for maintaining a constant temperature in the inner compartment of the incubator and this temperature is noted by a thermometer, the top of which projects above the top of the apparatus.

The oven is entirely surrounded with insulating material and is provided with two doors, the outer one being well insulated and the inner one is made of glass, all of the insulating material being finished in white enamel.

Tests covering 45 days were made, which showed that the cost of operating was small and that the fluctuation of temperature in the incubator, during this time, was a small fraction of one degree, notwithstanding the temperature of the room changed about 18 degrees every 24 hours.

The incubator is patented and manufactured by Scientific Materials Company, Pittsburg, Pa.

CHESTER F. FISHER.

LOSS OF ALCOHOL FROM LIQUIDS LOW IN ALCOHOL.

The attention of the writer was called to this subject by a controversy which occurred between him and a chemist employed by a brewing company as to the percentage of alcohol in a specimen of beer low in alcohol. The results are placed on record; they may be of some interest to other chemists who may have to deal with a similar piece of work.

Four specimens of the beer in question were analyzed and found to contain the following percentages of alcohol: 0.94, 0.83, 0.82 and 0.74. The beer was contained in the ordinary pint bottles closed with cork-lined tin caps crimped on. In getting the sample for analysis the caps were loosened just enough to be sprung off; about 110 to 125 cc. were withdrawn and the caps snapped back in place. The bottles were returned to the source from whence they came and were, after an interval of about thirty days, sent to a representative of the brewing company which had sold them. The alcohol was then redetermined by the other chemist who reported the percentages of alcohol in the same order as found in the original analysis but so much below the first figures that none of them exceeded 0.50 per cent. alcohol.

It appeared to the writer to be a matter of some interest to know whether the beer kept under these conditions was likely to lose a part of the alcohol as was indicated by these figures. Accordingly a bottle of the same brand of beer was analyzed March 15th and found to contain 0.96 per cent. alcohol. It was handled exactly as the other samples had been except that it was kept in the writer's office. On April 23rd the alcohol was redetermined, when it showed exactly the same percentage as before, 0.96. In spite, therefore, of the interval of thirty-nine days, no loss of alcohol could be detected. The bottle was kept as before until May 31st, a further period of thirty-eight days. During this time a small quantity of mould appeared in the liquid, though it did not smell sour. The mould was filtered out and the alcohol redetermined, when it was found to be 0.85 per cent. This difference is so slight that it may possibly be due to experimental error, but seems rather to indicate a very slight loss of alcohol. The results here given show, as an answer to the main question, that a liquid like the one under discussion does not, under the conditions named, lose more than a trace of alcohol in a period of over two and one-half months.

WILLIAM B. BENTLEY.

ATHENS, OHIO.

BUREAU OF STANDARDS ANALYZED SAMPLES.

A sample of acid open-hearth steel with 0.6 carbon is now ready for distribution, also a new sample of Bessemer 0.4 carbon in place of that hitherto supplied but now exhausted.

The next samples to be ready will probably be basic open-hearth 0.4 carbon (renewal) and a vanadium steel with about 0.2 per cent. V.

Certain iron ores are in preparation, but the dates of issue cannot be now given.

W. F. HILLEBRAND.

BOOK REVIEWS AND NOTICES.

Jahrbuch des Vereins der Spiritus-Fabrikanten in Deutschland, des Vereins der Störke Interesenter in Deutschland, and Vereins Deutscher Kartoppel-trockner. Neunter Jahr-

gang. 1909. Berlin: Verlagsbuchhandlung Paul Parey. 8vo. 594 pp.

This Jahrbuch which represents the interests of all the starch-products industries of Germany, covers with index advertisements and a register of sources of supplies of materials used in the industries indicated, 594 well-printed octavo pages of matter replete with information of value to those interested or engaged in these industries. As stated on an opening page it reaches all members of all the societies named and subscribers to the *Zeitschrift für Spiritus Industrie*, which in turn is the organ for publication of all that concerns the industries in question.

To offer here a detailed list of the subjects treated in the books would require too much time and space. It is sufficient to say that the contents represent excellently the progress made in the industries during the year in a chemical, physical and biological way. It presents lists and sometimes abstracts of articles published in the *Zeitschrift für Spiritus Industrie* and devotes much space to the work of the Institute für Gährungs-Gewerbe in Berlin and its very efficient officers and illustrates how carefully the interests of the industries are guarded in the scientific investigations and the work of instruction prosecuted in that institution. It is really headquarters for information regarding everything relating to the starch-products' industries and covers in its work and investigations culture of the potato, practically the sole raw material available in Germany for the starch-products' industries, the manufacture of starch, press-yeast alcohol, beer and vinegar, not only a scientific way but in practical directions as well. Thus the work extends beyond the analytical and research laboratories and lecture halls to the operation of the works, and includes study of fuel values by calorimetric tests, study and revision of manufacturing operations, where these appear to be defective or uneconomical yields, accounting, indeed, everything relating to the manufacture in such ways as to immediately aid in promoting progress in the industry. In addition the *Jahrbuch* presents detailed reports of the officers of the different departments of the Institute für Gahrungs-gewerbe and of what they have accomplished during the year and of the officers of the several societies, brief extracts from the material presented in the meetings of the societies and in many cases full reports of addresses made. These are, all of them, of an intensely practical character and constitute a valuable exposition of the condition of the industries in Germany and progress attained in them during the year. The *Jahrbuch* is a work which will fill a useful place in the library of every person interested in the starch-products' industries, for though "corn-products" are briefly treated there is to be found in the book much of value for application in the corn-products' industry in all its branches. WM. MCMURTRIE.

Tables of Properties, of over 1500 Common Inorganic Substances. By WILHELM SEGERBLOM, A.B. Cloth, 8vo., 144 pp. N. H.: Exeter Book Pub. Co. 1909.

This work gives the properties of the salts of the common metals and the acids, arranged according to the analytical groups. The non-metals (4 pages) and the rare metals (8 pages) are arranged in tables at the back of the book. The tables are arranged for the use of the student in qualitative analysis. The properties given include the color, luster, crystalline form, melting point, behavior when heated, solubility, and a few others. The book will undoubtedly prove of considerable utility as an auxiliary volume for the student in qualitative analysis.

Introduction to the Chemistry of Physics of Building Materials. By ALAN E. MUNBY. xx + 345 pp. Cloth, 8vo. New York: D. Van Nostrand Co. 1909. Price, $2.00.

The student of materials, the works superintendent who has not been technically educated and the general reader will find a good deal of information from several different sciences and arts grouped together in this volume. The scope of the volume can best be indicated by the chapters which are as follows: Chapter 1, Natural Laws and Scientific Investigations. 2. On Measurement and the Properties of Matter. 3. The Air and Combustion. 4. Heat: Its Nature and Measurement. 5. Heat and Its Effects on Materials. 6. Chemical Signs and Calculations. 7. Water and Its Impurities. 8. Sulphur and the Nature of Acids and Bases. 9. Coal and Its Products. 10. Outlines of Geology. 11. The Constituents of Stones, Clays and Cementing Materials. 12. Classification of Stones. 13. The Examination and Testing of Stones. 14. Brick and Other Clays. 15. Kiln Reactions and the Properties of Burnt Clays. 16. Plasters and Limes. 17. Cements. 18. Theories upon the Setting of Plasters and Hydraulic Materials. 19. Artificial Stone, Oxychloride Cement, Asphalt. 20. The Metals: Their General Properties and Occurrence. 21. Iron and Steel. 22. Other Metals and Alloys. 23. Tests upon and Strength of the Metals. 24. Timber. 25. Paints: General Characters—Oils, Thinners and Varnishes. 26. Paints: Their Solid Ingredients—Bases, Pigments and Driers. When information is drawn from so many fields and applications in so many directions are attempted, that data given must necessarily be brief. However, Mr. Munby's book will undoubtedly give an excellent general view of the fields covered to the reader, will help the student of the branches of knowledge treated and will serve as a starting point and incentive to further reading and study.

Practical Testing of Gas and Gas Meters. By C. H. STONE. Cloth, 8vo. v + 337 pp. New York: John Wiley & Sons. 1909. Price, $3.50.

Mr. Stone is Chief Inspector of Gas, Public Commission, 2nd District, New York, and speaks authoritatively on his subject. There was need for just such a book as this one, in view of the increasing public interest in public service corporations, the increasing tendency toward municipal regulation of such utilities, as well as for the needs of the chemist and engineer. Outside of the present volume, there is no modern American work on this subject. The scope of the book is shown by the following table of contents: Part 1: Chapter 1. The Photometer and Accessories. 2. Standards and Burners. 3. Candle-power Tests of Coal and Water Gas, Using Candles as Standards. 4. Photometric Work with Other Standards and Gases. 5. Interpretation of Results and Legal Requirements. Part 2: Chapter 1. Carbonic Acid and Sulphuretted Hydrogen. 2. Total Sulphur. 3. Other Impurities. 4. The Analysis of Gas. Part 3: Chapter 1. The Junker and Boys Calorimeters. 2. Other Instruments and Methods. 3. Consideration of Results. 4. Specific Gravity and Pressure. Part 4: Chapter 1. The Cubic Foot and Meter Prover. 2. The Method of Testing Meters.

The Smokeless Combustion of Coal in Boiler Plants. By D. T. RANDALL AND H. W. WEEKS. Bulletin 373, U. S. Geol. Survey. 8vo. pp. 188. Washington, Government Printing Office. 1909.

This most recent and excellent contribution to the smokeless combustion of coal will be welcomed by chemists and engineers everywhere. Bulletin 334, previously issued by the Survey, furnished a preliminary report on the same subject. Following the introduction, the present volume describes representative boiler plants burning coal without smoke, including plants with mechanical stokers and hand-fired furnaces. Following this are Some Observations at Geological Survey Fuel Testing Plants, Comparison of Methods of Supplying Air for Combustion, Influence of Volatile Matter in Fuel on the Smoke Problem, Central Heating Stations, General Conclusions on Smoke Abatement, and Bibliography. The Bulletin should be in the hands of all fuel chemists and engineers.

In their new catalogue of bacteriological apparatus, the Bausch & Lomb Optical Co. have added another interesting publication to their list. Aside from being very complete, the catalogue is of interest since it describes a new electric incubator, made in various sizes, which presents a number of unique features. These incubators are run on the main current without any auxiliaries whatever, and, being self-contained, they require no more space than does the ordinary laboratory incubator. The many advantages attending the use of electrically heated incubators are too apparent to call for consideration here.

Several forms of opsonic incubators, of hot air sterilizers, steam pressure sterilizers, and autoclave afford a wide range of choice, while the water baths and paraffin ovens listed answer all laboratory requirements. In addition to these items such accessories as thermo-regulators, thermometers and burners are given careful attention.

This catalogue may be had gratis by addressing the Company at Rochester, N. Y.

NEW BOOKS.

Industrial Chemistry.

Zur Bildung der Ozeanischen Salzablagerungen. By J. H. VAN'T HOFF. II Heft, gr. 8°. Braunschweig, 1909. Price, Mk. 4.00.

Mittelwerte von Temperatur und Salzgehalt Nach Hydrolog. Beobachtungen in Danischen Gewässern 1880–1907. By J. P. JACOBSEN. 26 s. og. 11 t. i. Fol. Kopenhagen, 1908. Price, Kr. 3.50.

Der Sauerstoffgehalt Des Meereswassers in Den Danischen Gewassern Innerh. Skagens. 5 t. 24 s. og. 5 t. i. Fol. Kopenhagen, 1908. Price, Kr. 2.00.

Boiler Feed Water: A Practical Treatise on Its Quality, Effects and Purification. By F. A. ANDERSON. 8°. London, 1908. Price, 6s.

Modern Power Gas Producer, Practice and Applications; A Practical Treatise Dealing with the Gasification of Various Classes of Fuels by the Pressure and Suction System of Producer. By H. ALLEN. 8°, 8+326 pp. New York, 1908. Price, $2.50.

Die Gasmaschine. Ihre Entwickelg., Ihre Heut. Bauart u. Ihr Kreisprozess. By R. SCHOTTLER. 5 A. Lex. 8. VIII, 491 S. m. 622 Fig. Berlin, 1909. Lnbd. Mk. 20.

Die Bedeutung der Kolloide für Die Technik. By K. ARNDT. 8vo, 34 pp. Dresden, 1909. Price, Mk. 1.

Foundry Practice: A Treatise on Molding and Casting in Their Various Details, Prepared for the Use of Students in the College of Engineering. University of Minnesota. By J. M. TATE and M. O. STONE. 12. y, 234 pp. New York, 1909. Price, $2.00.

Malmaterialienkunde Als Grundlage der Maltechnik. für Kunststudierende, Kunstler, Maler, Lackierer, Fabrikanten u. Handler. By A. EIBNER. Gr. 8°, xxiii+480 S. Berlin, 1909. Lnbd. Mk. 13.60.

Der Kunststein. Handbuch f. Die Gesamte Kunststein-Industrie. Umfassend Die Gewinnung Der Rohmaterialien. Die Bereitg. u. Verarbeitg. der Mortel, Die Anfertigg. Der Formen u. Modelle, Sowie Die Herstellg. u. Behandlg. der Kunstl. Steine. Nebst E. Anh. Ub. Die Anlage u. Leitg. E. Kunststeinfabrik. By A. BOHNAGEN. Lex. 8, viii+150 S. m. 146 Abb. Leipzig, 1909. Price, Mk. 6; gebd., 7.50.

Ausfuhrliche Anleitg. f. Die Herstellung und Verwendung V. Kunstholz Resp. Steinholz Aus Verschiedenen Rohmaterialien u. Billigen Abfallstoffen. By K. MULLER. 3. A. Gr. 8. 199 S. m. Abb. Gommern, 1909. Price, Mk. 5.00.

Uber Das Brennen V. Porzellan. (Aus: "Tonindustrie-Ztg.") By A. HEINECKE. 8°, 20 S. Berlin, 1908. Price, Mk. 1.

Der Praktische Glashuttentechniker. By J. BALDERMANN. Gr. 8°, 422, Vi. S. u. 26 Taf. in 51 × 68 cm. Mappe 35,5 × 26.5 cm. Leipzig, 1909. Price, Mk. 250.00.

Verdampfen, Kondensieren u. Kuhlen. Erklarungen, Formeln. u. Tabellen f. Den Prakt. Gebrauch. By E. HAUSBRAND. 4 A. xx+426 S. m. 36 Fig. u. 74 Tab. Berlin, 1909. Lnbd. Mk. 10.

Die Deutsche Spiritusindustrie. Eine Wirtschaftliche Monographie Unter Besonderer Berucksichtigung Des Einffusses Der Technik. By L. WASSERMANN. 8, x+218 S. Leipzig, 1909. Price, Mk. 5.

Rezeptbuch für Destillateure. Reichhaltigste Sammlung Ueber 300 Moderner Rezepte. By H. GOETTLER. Neustadt, 1909. Price, gebd., Mk. 25.

Leitfaden für Die Biologische Untersuchung und Begutachtung von Bierwurze, Bierhefe, Bier und Brauwasser für Die Betriebskontrolle und Die Hefereinzucht. By H. WILL. München, 1909. Lnbd. Mk. 13.20.

Chemical Technology and Analysis of Oils, Fats and Waxes. By J. LEWKOWITSCH. 4th ed., entirely rewritten and enlarged. 3 vols., 1909, 8vo. Vol. I, 540 pp., 54 figs.; Vol. II, 786 pp., 20 figs.; Vol. III, 379 pp., 28 figs. London and New York: Macmillan Co. Price, 2£ 10s.

Systematic Treatment of Metalliferous Waste. By L. PARRY. 8vo, 121 pp., 8 ill., 1909. London: *The Mining Journal.* Price, 5s. net.

Das Ammoniak und Seine Verwendungen. By J. GROSSMANN. 8vo, 103 pp., 7 ill., 1908. Halle a/S: W. Knapp. Price, Mk. 3.60.

Adressbuch der Deutschen Gummi-, Guttapercha- und Asbest-Industrie. VII, Ausg., 1909. Berlin: Verlag Union, Deutsche Verlagsgesellsch.

Analytical Chemistry

Die Untersuchung von Eisengallustinten. By F. W. HINRICHSEN. (Die chem. Analyse. Hrsg. v. B. M. Margosches. 6 Bd.) Lex.-8. 140 S. m. 7 Abb. u. 33 Tab. Stuttgart, 1909. Price, Mk. 4.40; gebd., 5.00.

Anleitung Zur Chemischen u. Physikalischen Untersuchung der Spreng- u. Zündstoffe. (Aus: "Post's chemisch-techn. Analyse.") By H. KAST. Gr. 8, vii+139 u. 14 S. m. Fig. Braunschweig, 1909. Price, Mk. 4.20.

Farbenchemisches Praktikum. Zugleich Einführung in Die Farbenchemie u. Farbereitechnik. By R. MOHLAU u. H. TH. BUCHERER. Gr. 8, x+374 S. m. Taf. u. Mustern. Leipzig, 1909. Lnbd. Mk. 12.

Practical Testing of Gas and Gas Meters. By C. H. STONE, B.S., M.S., 1909. 8vo, x+337 pp., 51 figs., cloth. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. Price, $3.50.

Laboratory Manual of Dyeing and Textile Chemistry. By J. MERRITT MATTHEWS, PH.D., 1909. 8vo, xii + 363 pp. New York: John Wiley & Sons. London: Chapman & Hall. Price, cloth, $3.50.

Manual of Volumetric Analysis. By HENRY W. SCHIMPF, PH.G., M.D. For the use of pharmacists, sanitary and food chemists as well as for students in these branches. 1909, 8vo, xx + 725 pp., 102 figs. New York: John Wiley & Sons. London: Chapman & Hall. Price, cloth, $5.00.

Pharmaceutical Chemistry.

Handbuch der Pharmakognosie. By A. TSCHIRCH. Abtlg. Leipzig, 1909. Price, Mk. 16.

Grundrib der Klinschen Bluntuntersuchung. By K. v. MULLERN. Lex.-8, vi+178 S. m. 5 Abb., 6 Taf. u. 6 Bl. Erklargn. Wien, 1909. Price, Mk. 8.

Drug Legislation in the United States. Revised to July 15, 1908. By LYMAN F. KEBLER, Chief Division of Drugs. 343 pp. (Bulletin 98, Revised, Part 1, Bureau of Chemistry). Price, 35 cents.

Textile Chemistry and Paper.

Durability and Economy in Paper for Permanent Records. Including paper specifications by F. P. VEITCH. 51 pp., 4 figs. (Report No. 89, Office of the Secretary.) Price, 15 cents.

Ueber Technologische Veränderung der Leinengarne Durch Den Bleichprozess. By H. SCHNEIDER. Lex.-8, 38 S. m. Abb. Leipzig, 1908. Price, Mk. 2.

Flachsbau u. Flachsindustrie in Holland, Belgien u. Frankreich. (Berichte Ub. Landwirtschaft. 9 Heft). By J. FROST. Lex 8, v+142 S. m. 20 u. 25 Abb. Berlin, 1909. Price, Mk. 3.80.

Die Papierindustrie der Welt in Ihrer Entstehung u. Heutigen Bedeutung. (Kommerzielle Berichte. Hrsg. V. K. K. Osterr. Handels-Museum. Nr. 13). By F. KRAWANY. Lex. 8, 78 S. Wien, 1909. Price, Mk. 2.00.

The Textile Fibers, Their Physical, Microscopical and Chemical Properties. By J. MERRITT MATTHEWS, PH.D. (formerly head of Chemical and Dyeing Department, Philadelphia Textile School). 2nd ed., rewritten. 8vo, viii+480 pp., 127 figs. New York: John Wiley & Sons. London: Chapman & Hall. Price, cloth, $4.00.

The Dyeing and Cleaning of Textile Fabrics: A Handbook for the Amateur and the Professional. By F. A. OWEN, B.S. Based partly on notes of H. C. STANDAGE. 1909, 12 mo., vi+253 pp. New York: John Wiley & Sons. London: Chapman & Hall. Price, cloth, $2.00.

Agricultural Chemistry.

The Physical Properties of Soils. By A. G. MCCALL. 8. London, 1909. Price, 2s. 6d.

Economic Loss to the People of the United States through Insects that Carry Disease. By L. O. HOWARD, Entomologist and Chief of Bureau. 40 pp. (Bulletin 78, Bureau of Entomology). Price, 10 cents.

The Feeding Value of Cereals, as Calculated from Chemical Analyses. By JOSEPH S. CHAMBERLAIN, Chief, Cattle-food and Grain Laboratory, Miscellaneous Division in Collaboration with the Bureau of Plant Industry. 64 pp., 46 tables. (Bulletin 120, Bureau of Chemistry.) Price, 10 cents.

The Rôle of Oxidation in Soil Fertility. By OSWALD SCHREINER and HOWARD S. REED. 52 pp. (Bulletin 56, Bureau of Soils.) Price, 10 cents.

The Isolation of Harmful Organic Substances from Soils. By OSWALD SCHREINER and EDMUND C. SHOREY. 53 pp., 4 pls. (Bulletin 53, Bureau of Soils.) Price, 15 cents.

Chemical Studies of American Barleys and Malts. By J. A. LECLERC, Physiological Chemist, and ROBERT WAHL, Special Agent. 75 pp., frontispiece. (Bulletin 124, Bureau of Chemistry.) Price, 20 cents.

Food Chemistry.

A Study of the Methods of Canning Meats, with Reference to the Proper Disposal of Defective Cans. By C. N. MCBRIDE, Bacteriologist, Biochemic Division. 18 pp., 1 fig. (Reprint from *An. Rpt. B. A. I.*, 1907.)

Leitfaden f. Fleischbeschauer. Eine Anweisg. f. Die Ausbildg. Als Fleischbeschauer u. f. Die Amtl. Prufgn. By R. OSTERTAG. 10 A., gr. 8°, xiv+281 S. m. 190 Abb. Berlin, 1909. Lnbd. Mk. 6.50.

Miscellaneous.

Lehrbuch der Organischen Chemie. 2. A. I. Bd. Allgem. Tl. Verbindungen der Fettreihe. 2. Tl. Mehrwert. Abkommlinge der Aliphat. Kohlenwasserstoffe. Cyanverbindungen u. Kohlensaurederivate. By V. MEYER u. P. JACOBSON. 1. Abtlg., gr. 8, 288 S. m. Fig. Leipzig, 1909. Price, Mk. 7.50.

Bibliographie Neuer Erscheingn. Aller Lander Auf Dem Gebiete der Naturgeschichte u. der Exakten Wissenschaften. Naturae novitates. 31. Jahrg., 1909, 26 Nrn., 8. Berlin, 1909. Price, Mk. 4.

Terpene u. Campher. Zusammenfassung Eigener Untersuchgn. Auf. dem Gebeit der Alicycl. Kohlenstofferbindgn.

By O. WALLACH. Gr. 8, xxii+576 S. Leipzig, 1909. Price, Mk. 18; Hibfrz., Mk. 20.50.

Tables of Properties, of Over Fifteen Hundred Common Inorganic Substances. By WILHELM SEGERBLOM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. 1909, 8vo, x+144 pp. Exeter, N. H.: Exeter Book Pub. Co. Price, cloth, $3.00.

Colloids and the Ultramicroscope. By DR. RICHARD ZSIGMONDY. Authorized translation by JEROME ALEXANDER, M.Sc. 1909, 8vo, xiii + 245 pp., ill. with line cuts and 2-color plates. New York: John Wiley & Sons. London: Chapman & Hall. Price, cloth, $3.00.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN CHEMICAL SOCIETY, DETROIT MEETING.

The very successful Detroit meeting of the society will be fully reported in the August number of this Journal. In particular the secretaries of the Division of Industrial Chemists and Chemical Engineers and the Division of Fertilizer Chemists will furnish special reports of the meetings of those Divisions. In addition many of the papers read at Detroit will appear in these columns during succeeding months.

PROGRAM OF THE FORTIETH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY HELD AT DETROIT, MICHIGAN.

From Tuesday June 29 to Friday July 2, 1909

MONDAY, JUNE 28TH.

8 P.M.—

Hotel Ponchartrain.

MEETING OF THE COUNCIL.

TUESDAY, JUNE 29TH.

Central High School, Third Floor.

10 A.M.—

Address of Welcome, Dr. F. T. F. Stephenson, President Society Detroit Chemists.

Response, Dr. W. R. Whitney, President American Chemical Society.

10.30 A.M.—

Meetings of Divisions. For program see following pages.

1 P.M.—

Recess for lunch.

2.30 P.M.—

Continuation of morning meetings.

8 P.M.—

Theater party for ladies.

Smoker at Harmonic Hall, corner Wilcox and Centre streets, complimentary to the visiting chemists, by the Society of Detroit Chemists. An invitation is extended to all members of the American Chemical Society and their guests to be present.

WEDNESDAY, JUNE 30TH.

9.30 A.M.—

Central High School.

Meetings of Divisions.

1 P.M.—

Recess for lunch.

2.30 P.M.—

Hotel Ponchartrain.

Wednesday afternoon and evening, the members, ladies and visitors will be entertained by Parke, Davis & Co. This entertainment will consist of the inspection of their laboratories in the afternoon, luncheon in the evening and moonlight ride on the river after luncheon. This should be a very instructive and enjoyable afternoon and evening for all those who attend, and no one who has ever before enjoyed the well-known hospitality of Parke, Davis & Co. will fail to take advantage of this feature. This plant, manufacturing pharmaceutical preparations of all kinds, is one of the largest and most completely equipped in the world.

THURSDAY, JULY 1ST.

8.25 A.M.—

Thursday morning the attending members and visitors will leave for Ann Arbor on invitation of the Regents of the University of Michigan. The regular train leaves at 8.25 o'clock *via* Michigan Central. If enough members signify in advance their intention of attending, a special train may be provided. The party will return to Detroit by the regular train leaving at 4.50 P.M., unless a special train is obtained. The Regents of the University of Michigan will provide a noonday lunch.

10.00 A.M.—

General Meeting, Barbour Gymnasium. The following addresses will be given:

F. K. Cameron (for Agricultural and Food Division). The Dynamic View Point of Soils.

H. E. Howe (for Industrial Division). Optical and Quartz Glass: Their Chemical and Physical Properties.

Wilder D. Bancroft (for Division of Physical and Inorganic Chemists). The Chemistry of Phosphorescing Solids.

Alexander Smith (for Section of Chemical Education). The Place of Chemistry in the American College.

2.00 P.M.—

General Meeting. Barbour Gymnasium.

Section of Chemical Education.

Papers will be presented as follows:

S. Lawrence Bigelow. "Some Ideals, Some Difficulties, and a Compromise for a First Course in Chemistry."

Arthur John Hopkins. "A First College Course in Chemistry."

Lauder W. Jones. "College Chemistry beyond the Elementary Course."

Harry McCormack. "Laboratory Instruction in Industrial Chemistry."

Norman A. Dubois. "Teaching by the Lecture System."

8.00 P.M.—

Subscription Dinner. Hotel Ponchartrain.

FRIDAY, JULY 2ND.

9.30 A.M.—

Adjourned meetings of Sections and Divisions.

Excursions may also be arranged for Friday morning if divisional programs have been completed.

1.30 P.M.—

Excursions to manufacturing plants. Members should register their choice of excursions at the registration desk, or with Dr. F. T. F. Stephenson, as early in the meeting as possible.

List of Plants Open for Visitation.

Acme Lead & Color Works. Paints, White Lead by new process.

Morgan & Wright. Auto Tires and Mechanical Rubber

Detroit Salt Co. Rock Salt Mine, 800 feet deep.

Murphy Ice Co. Distilled water, artificial ice. Ozonizing plant in connection.

Peoples' Ice Co. Artificial ice plant.

Packard Automobile Co. "Ask the man that has one."

Detroit City Gas Co. Manufacturers Illuminating gas.

Cadillac Motor Car Co. Auto Manufacturers.

The Herpicide Co. "Going, Going, Gone."

Goebel Brewing Co. Annual capacity 350,000 barrels.

Hiram Walker & Sons. Distillery of "Canadian Club."

American Electric Heater Co. Largest electric heating apparatus plant in America.

Hoskins Mfg. Co. Pyrometers and Electric Furnaces.

Sibley Quarry Co. Limestone and Sand-lime bricks.

Peninsular Engraving Co. Engravers and Printers.

The Clark Wireless Telegraphy Co. Manufacturers wireless equipment.

Berry Brothers. Varnish manufacturers.

Detroit Iron and Steel Co. Blast Furnace.

DIVISION OF AGRICULTURAL AND FOOD CHEMISTS.

W. D. Bigelow, *Chairman.*

W. B. D. Penniman, *Secretary.*

PAPERS.

1. A. B. Adams. "The Distillation of Whiskey." (30 min.)

2. L. L. Van Slyke. "The Chemistry of Milk." (30 min.)

3. L. L. VanSlyke and A. W. Bosworth. "Volumetric Method for Determining Casein in Milk."

4. E. V. McCollum and W. E. Tottingham. "A Chemical Study of the Interaction of Fermenting Manures and Ground Rock Phosphate. (10 min.)

5. J. Pearce Mitchell. "Determination of Nitrates in Potable Waters with High Chloride Content."

6. J. Pearce Mitchell. "Normal Chloride Content of Surface Waters on the San Francisco Peninsula."

7. Hermann C. Lythgoe. "The Relation between the Calcium and the Fat Content of Cream." (5 min.)

8. Edmund Clarke. "The Determination of Benzoic Acid in Food Products."

9. G. H. Failyer and W. H. Waggaman. "The Estimation of Organic Matter in Soils." (10 min.)

10. F. K. Cameron and W. O. Robinson. "The Relation of the Iron Content to the Color of Soils." (10 min.)

11. H. E. Patten. "The Relation of Moisture Content to the Heat Conductance of Soils." (15 min.)

12. C. G. Hopkins. "The Element System of Nomenclature in Soil Chemistry." (20 min.)

13. G. S. Fraps. "The Interpretation of Soil Analyses with Respect to Phosphoric Acid. (10 min.)

14. G. S. Fraps. "The Potash of the Soil." (10 min.)

15. G. S. Fraps and N. C. Hamner. "The Oxidation of Organic Matter in the Soil." (10 min.)

16. G. S. Fraps. "The Constants of Pecan Oil." (10 min.).

17. W. D. Bigelow and M. C. Albrech. "The Determination of Sugar in Chocolate." (15 min.)

18. S. H. Ross. "A Modification of the Winton Lead Number in Maple Syrup." (10 min.)

19. E. M. Chace and H. S. Bailey. "The Analysis of Lemon Oil." (15 min.)

20. C. S. Hudson. "The Hydrolysis of Salicyn by the Enzyme Emulsion." (15 min.)

21. F. W. Morse and B. E. Curry. "The Stimulating Effect of Calcium Salts on Clover and Wheat Seedlings."

22. A. L. Sullivan. "The Determination of Caffein in Coffee." (10 min.)

23. B. H. Smith. "Examination of Dried Fish." (10 min.)

24. R. W. Balcom. "Examination of Vinegar." (15 min.)

25. Edward Bartow. "Composition and Treatment of Lake Michigan Water." (5 min.)

BIOLOGICAL CHEMISTRY SECTION.

Samuel C. Prescott, *Chairman.*

PAPERS.

1. H. S. Grindley and H. H. Mitchell. "A Study of the Food Requirements of Group of Twenty-four Men."

2. H. S. Grindley. "Urinary Creatinine of Men of Health." Lantern slides. (15 min.)

3. F. W. Gill and H. S. Grindley. "The Determination of Urea in Urine." Lantern slides. (10 min.)

4. A. D. Emmett and H. S. Grindley. "Animal Nutrition. The Chemical Composition of the Wholesale Cuts of Beef from Three Animals." Lantern slides.

5. Waldemar Koch. "A Review of Methods for the Estimation of Fat in Tissues."

6. P. F. Trowbridge. "The Determination of Phosphorus in Flesh."

7. C. R. Moulton and P. F. Trowbridge. "The Composition of Fat of Beef Animals on Different Planes of Nutrition."

8. P. F. Trowbridge and F. W. Woodman. "Changes in the Composition of the Skeleton of Beef Animals."

9. Earl B. Phelps. Title to be announced.

FERTILIZER CHEMISTRY SECTION.

F. B. Carpenter, *Chairman.*

J. E. Breckenridge, *Secretary.*

PAPERS.

1. J. E. Breckenridge. "Potash Tests in Commercial Fertilizer."

2. F. B. Porter. "The Measurement of Crude Sulphuric Acid."

3. R. H. Fash. "The Corrosive Action of Alkaline Tank Water upon an Evaporator and a Remedy." (10 min.)

4. R. H. Fash. "The Use of Wood Ashes in Commercial Fertilizers." (5 min.)

5. J. M. McCandless. "Preparation and Neutralization of the Ammonium Citrate Solution."

6. G. S. Fraps. "The Needs of Texas Soils for Fertilizers."

7. P. D. Youngblood. "The Scientific Preparation of Phosphate Samples for Chemical Analysis."

8. G. A. Farnham. "The Effect on Insoluble Phosphoric Acid when Litmus, Corallin and Cochineal Are Used in Preparing Solution of Ammonium Citrate." (10 min.)

9. Burt L. Hartwell. "The Availability of Certain Nitrogenous Manures."

10. Carlton C. Jones. "Moisture in Phosphate Rock of the Pacific." (5 min.)

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

A. D. LITTLE, *Chairman*.

B. T. B. HYDE, *Secretary*.

PAPERS.

1. C. K. Francis. "Limitations of Use of Starch as an Accelerator in the Fusion Method."

2. Charles P. Fox. "The Technical Determination of Caoutchouc in Guayule." (10 min.)

3. Clarence Riegel. "Laboratory Reagents and C. P. Chemicals."

4. Louis A. Fischer and N. S. Osborne. "Standard Hydrometers." (20 min.)

5. C. W. Waidner. "The Temperature Work of the Bureau of Standards." (20 min.)

6. Edward DeMille Campbell. "On the Influence of the Temperature of Burning on the Rate of Hydration of Magnesium Oxide."

7. H. B. Bishop. "The Electrotitrimeter." (20 min.)

8. W. C. Geer. "The Present Status of the Chemistry of India Rubber." (By title.)

9. Arthur G. Smith. "Free Lime in Portland Cement—A Mill Study."

10. J. E. Moore. "The Inspection of Material."

11. W. C. Ebaugh. "Bag-house Treatment of Blast Furnaces and Roaster Gases."

12. F. E. Gallagher. "Hygienic Significance of Sulphur in Illuminating Gas."

13. Alfred H. White. "The Destructive Distillation of Coals for Illuminating Gas; An Experimental Study."

14. L. P. Kinnicutt. "The Determination of Fat and Soap in Sewage Effluents."

15. G. W. Sargent. "Observations upon the Direct Determination of Carbon in Various Steels."

16. Robert Spurr Weston. "Determination of Nitrates in Potable Water."

17. S. W. Parr and W. F. Wheeler. "The Ash of Coal and Its Relation to Actual or Unit Coal Values."

18. S. W. Parr, Brainerd Mears and D. L. Weatherhead. "The Analysis of Asphalt and Asphaltic Compounds."

19. S. W. Parr and W. F. Wheeler. "A Series of Parallel Determinations with the Mahler and Parr Calorimeters."

20. Chas. H. Herty and E. J. Newell. "Further Application of the Specific Gravity Method for Determining Fat."

21. Chas. H. Herty. "Some New Extractives for Use in Determining Fats."

22. Isador Ladoff. "Some Technical Applications of Titanium."

23. William Brady. "The New Brady Gas Apparatus."

24. A. B. Davis. "A New Oil Gas Producer."

25. L. Auchy. "Manganese in Steel"—a note.

26. Roger C. Griffin. "The Analysis of Lead Arsenate for Water-soluble Impurities."

27. N. H. Claussen. "The Bouquet of Wine and Beer."

28. A. Nilson. "The Importance of Pedigree Cultures of Barley for Brewing Purposes."

29. Warren K. Lewis. "The Decomposition of Calcium Carbonate by Steam."

30. Wm. H. Walker and Warren K. Lewis. "The Structure of Tin Plate as Determined by Its Method of Manufacture."

31. Wm. H. Walker and Warren K. Lewis. "Paint and Varnish Coatings as Accelerators in the Corrosion of Metals."

32. Wirt Tassin. "Convenient Illuminator for the Microscopic Examination of Opaque Objects." (5 min.)

33. Wirt Tassin. "Copper Clad Steel—a Recent Metallurgical Product." (15 min.)

34. P. W. Shimer. "A Simplified Combustion Crucible."

35. David Bloom. "Note on a Convenient Condenser for Extractions."

36. H. G. Martin. "Barium and Sulphur in Fluorspar."

37. Theo. P. Holt. "Cyanidation of Silver Minerals."

38. John T. Baker. "The Preparation of Sodium Oxalate for Use in Standardizing."

39. Charles A. Davis. "Commercial Aspects of Peat as a Source of Chemical Products."

40. A. C. Houghton. "Estimation of Pyridine in Aqueous Ammonia."

41. G. G. Wheat. "Studies in the Solubility of Portland Cement."

42. O. T. Joslin. "The Twitchell Process of Glycerine Recovery as Compared with the Ordinary Soap Kettle Saponification."

PHARMACEUTICAL CHEMISTRY SECTION.

A. B. STEVENS, *Chairman*.

PAPERS.

1. Frank O. Taylor. "Aconite."

2. W. A. Pearson. "Chemical Manipulations and the Valuation of Results."

3. Charles E. Parker. "A New Form of Separator."

4. Charles E. Parker. "Notes on the Determination of Morphine."

5. Azor Thurston. "Tincture of Iodine."

6. Henry C. Fuller. "Two Important Alkaloidal Reactions."

7. Henry C. Fuller and Lyman F. Kebler. "The Purity of Glycerin."

8. B. L. Murray. "The Need of Methods of Analysis of Pharmacopoeial Articles."

9. A. B. Stevens. "Chemical and Physiological Assay of Aconite."

10. F. B. Kilmer. "The Assay of Medicated Plasters."

11. Edward Kremers. "Pharmacopoeial Ash Standards."

12. Edward Kremers. "Note on the Curing of Burdock Root."

13. L. F. Kebler and B. Herstein. "Investigation of Glacial Phosphoric Acid."

14. B. Herstein. "The Estimation of Molybdenum."

DIVISION OF ORGANIC CHEMISTS.

R. S. CURTISS, *Chairman*.

RALPH H. MCKEE, *Secretary*.

PAPERS.

1. Wm. McPherson and Howard J. Lucas. "A Study of Hydrazino-compounds." (5 min.)

2. William McPherson and Cecil Boord. "A General Method for Preparing the Pure Sulphates of Hydroxyazo Compounds." (5 min.)

3. Wm. L. Evans and E. J. Witzemann. "Preparation and Oxidation of *m*-Nitrobenzoylformaldehyde." (10 min.)

4. Alfred Tingle. "Hydrogen Polysulphide as a Reducing Agent." (5 min.)

5. M. T. Bogert and A. H. Kropff. "On Some Amino and Nitro Amino Derivatives of Benzoic, Meta Toluic and Meta Phthalic Acids." (15 min.)

6. M. T. Bogert and R. A. Gortner. "On 2-Methyl-3-amino-4-quinazolone and Certain of Its Derivatives." (10 min.)

7. M. T. Bogert and R. A. Gortner. "On Oxalylanthranilic Compounds and Some Quinazolines Derived Therefrom." (10 min.)

8. J. Bishop Tingle and B. F. Parlett Brenton. "Intramolecular Rearrangement of Phthalamidic Acids." (3 min.)

9. J. Bishop Tingle and B. F. Parlett Brenton. "Action of Amines on Dicarboxylic Acids of the Aliphatic and Aromatic Series." (3 min.)

10. J. Bishop Tingle and S. J. Bates. "Aliphatic Phenylamidic (Anilic) Acids." (5 min.)

11. J. Bishop Tingle and C. E. Burke. "Action of Nitranilines on Certain Organic Acids." (3 min.)

12. Julius Stieglitz. "Stereoisomeric Nitrogen Derivatives —Chlorimido-ketones." (10 min.)

13. Oswald Schreiner and Edmund C. Shorey. "The Isolation of Some Further Organic Substances from Soil Humus: (1) Alpha-hydroxystearic Acid. (2) Paraffinic Acid. (3) Liquid Fatty Acids."

14. M. Gomberg and L. L. Van Slyke. "The Action of Molecular Silver and Silver Sulphate on Ortho-brominated Triphenylcarbinolchlorides." (10 min.)

15. M. Gomberg and L. P. Kyriakides. "The Constitution of the Double Salts of Triphenylcarbinolhalides with Metal Halides." (5 min.)

16. Richard S. Curtiss. "Condensations in the Mesoxalic Ester Series." (5 min.)

17. P. F. Trowbridge and C. K. Francis. "Glycogen Content of Beef Flesh."

18. F. B. Allan. "The Barium Salts of Phthalic Acid."

19. F. B. Allan and C. G. Allin. "A Third Methyl Ester of Phthalic Acid."

20. F. B. Allan and C. H. Robinson. "The Preparation and Properties of Phthalyl Cyanide."

21. Sidney Nirdlinger. "The Rearrangement of Tautomeric Salts." (15 min.)

22. M. T. Bogert and A. H. Kropff. "Researches on Quinazolines (24th paper). On 6-Methyl-7-aminoquinazolones, 7-Nitroquinazolone-6-carboxylic Acids, and 1,3,7,9-Naphthotetrazines." (15 min.)

23. R. R. Renshaw. "Simple L-B Diglycerides."

24. R. R. Renshaw. "Choline, I."

25. R. R. Renshaw and K. N. Atkins. "Bactericidal Properties of Lecithin."

26. Nicholas Knight and Layton Gouldin. "Investigation of the Fruit of the Rose." (8 min.)

27. W. A. Noyes, E. E. Gorsline and Luther Knight. "Molecular Rearrangements in the Camphor Series."

28. Edward Kremers. "Some Effects of Solvents Containing Hydroxy Groups on True Nitroso Compounds."

29. W. C. Arsem. "A New Synthesis of Alkyl Halides."

DIVISION OF PHYSICAL AND INORGANIC CHEMISTS.

Charles H. Herty, *Chairman.*

Wilder D. Bancroft, *Secretary.*

PAPERS.

1. W. R. Whitney. "The Physical Chemistry of Certain Arrowheads." (12 min.)

2. E. C. Franklin. "The Electrical Conductivity of Concentrated Solutions." (15 min.)

3. W. D. Bancroft. "The Development of Positives after Short Exposures." (12 min.)

4. J. W. Turrentine. "Rapid Electro-analysis with Graphite Cathode Dish."

5. F. K. Cameron. "Effects of Surfaces on Reactions."

6. A. W. Browne and T. W. B. Welsh. "Behavior of the Higher Hydronitrides in Liquid Ammonia." (12 min.)

7. C. H. Herty. "Valence—What Is It?" (12 min.)

8. W. Lash Miller. "The Effect of Salts on the Toxicity of Phenol Solutions." (10 min.)

9. R. B. Moore. "The Formation of Carbon Dioxide in Solutions of Thorium Nitrate."

10. E. P. Schoch, Ethel Sykes, D. J. Brown and A. G. Koenig. "Observations on the Use of the Auxiliary Electrode in Rapid Electrolytic Analysis." (7 min.)

11. D. M. Lichty. "Some Physical Properties of Sulphur Trioxide." (15 min.)

12. T. W. Richards and H. H. Willard. "The Atomic Weight of Silver." (12 min.)

13. W. O. Robinson and W. H. Waggaman. "Basic Magnesium Chlorides." (5 min.)

14. F. K. Cameron and W. O. Robinson. "Condensation of Solvent in Dilute Solutions of Electrolytes." (10 min.)

15. E. C. Bingham. "The Relation between Fluidity and Vapor-pressure." (15 min.).

16. V. J. Skillman. "The Tensile Strength of the Zinc-Aluminum Alloys." (10 min.)

17. E. D. Campbell and C. E. Griffin. "On the Volumetric Determination of Vanadium and Uranium."

18. B. E. Curry. "The Zinc-antimony Alloys."

19. R. C. Snowdon. "The Reduction of Nitrobenzene by Iron."

20. E. P. Schoch and C. P. Randolph. "The Behavior of the Iron Anode in Various Electrolytes." (7 min.)

21. Charles James. "The Rare Earth Bromates." (Second paper.)

22. Charles L. Parsons and G. J. Sargent. "On Some Organic Compounds of Beryllium."

23. H. N. McCoy. "Organic Amalgams." (12 min.)

24. H. N. McCoy. "The Chemical Properties of the Radioactive Products of Thorium."

25. Geo. E. Edelen. "A New Apparatus for Regulating the Supply of Heating Mediums for Scientific and Similar Apparatus."

26. S. Lawrence Bigelow. "The Size of Pores in Membranes and Osmotic Effects." (10 min.)

27. G. R. White. "Corrosion of Cadmium in Nitrate Solutions." (10 min.)

28. H. C. Cooper. "Lead Silicates." (10 min.)

29. W. C. Arsem and Harold Rush. "The Melting Point and Volatility of Chromium."

30. W. C. Arsem. "Electric Vacuum Furnace Installa-

tions in the Research Laboratory of the General Electric Company."

31. W. C. Arsem. "The Salts of Dichlor-tungstic Acid."

32. W. C. Arsem. "Oxalo-molybdic Acid and its Salts."

33. J. E. Mills. "Molecular Attraction." (15 min.).

34. J. E. Mills. "The Internal Heat of Vaporization."

35. M. A. Rosanoff and B. S. Merigold. "On the Kinetics of Certain Inorganic Reactions in Heterogeneous Media."

36. Otis D. Swett. "Solvents for Use with the Munroe Crucible."

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

First Semi-annual Meeting, Brooklyn, June 24–26, 1909.

PROGRAM.

THURSDAY, JUNE 24TH.

9.30 A.M.—

Addresses of welcome.

To the City of New York. Comptroller Herman A. Metz.

To the Institute. Prof. Irving W. Fay.

10 A.M.—

"Limits of Efficiency of the Power Gas Producer." Prof. W. D. Ennis.

"The Utilization of Low-grade Fuels in the United States." O. K. Zwingenberger.

"Creosote Oil from Water Gas Tar." President S. P. Sadtler.

12 A.M.—

Business Session.

12.45 P.M.—

Lunch at St. George Hotel.

2 P.M.—

"Some Experiments on Case Hardening of Steel with Gases." J. C. Olsen.

"Automatic Acid Egg." Richard K. Meade.

"The Centering of Great Industries in the New York Metropolitan District." Chas. F. McKenna.

"Methods of Clay Control." J. G. Dean.

Adjournment.

7 P.M.—

Subscription Dinner at Brighton Beach Hotel, $2.00.

FRIDAY, JUNE 25TH.

EXCURSIONS.

It is understood that Chemical Engineers who are allied with competing companies will not attend these excursions unless they declare themselves and can extend the same courtesy of inspection from their own plants.

9.30 A.M.—

Excursion to the Atlantic White Lead and Linseed Oil Works, foot of Gold St., Brooklyn, N. Y. (The manufacture of white lead, linseed oil, lead pipe and sheet lead.)

11.30 A.M.—

Through the courtesy of the National Lead Company, their steam lighter "Atlantic" will convey the members of the Institute and their guests up the Hudson River.

1 P.M.—

Excursion through the Edgewater plant of the Corn Products Refining Company. (The manufacture of glucose, starch and corn by-products.)

3.30 P.M.—

Excursion through the Edgewater plant of the Warner Sugar Refining Company.

5.30 P.M.—

Return trip on the steam lighter "Atlantic."

Luncheon and refreshments will be served on the boat, for which a charge of $1.50 will be necessary.

As the capacity of the boat is limited, application should be made as early as possible to the Secretary for tickets. Members purchasing tickets for friends must give name and official position of persons for whom tickets are purchased.

SATURDAY, JUNE 26TH.

EXCURSIONS.

9.30 A.M.—

Excursion to the Standard Oil Company's plant at Bay Way, N. J. (The refining of petroleum and by-products.)

Through the courtesy of the Standard Oil Co., the members of the Institute and their guests will be conveyed by a steamboat to Bay Way, N. J. The boat will leave Pier 4, North River, at 9.30 A.M.

The plant of the Consolidated Gas Co. at Astoria, L. I., may be visited during the afternoon, the trip being made *via* the new Blackwell's Island Bridge.

TWENTY-SIXTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By direction of the Executive Committee of the Association, the Twenty-sixth Annual Convention will be held at Denver, Colorado, August 26–28th, inclusive, 1909. As the meeting of the Association of State and National Food and Dairy Departments will be held at the same place from August 24–27th, and the Association of Agricultural Colleges and Experiment Stations meets at Portland, Oregon, August 18–20th, it appears opportune to join forces with these two organizations and give to our Western members the advantage of a meeting in that section.

A supplementary notice will be issued later in regard to headquarters, hotel rates, program of the meeting, etc.; at present the attention of the members is called to the following points:

RAILWAY RATES.

Pending more definite information the following is quoted from a letter received from the secretary of the Trunk Line Association, New York City:

* * * Regular summer tourist fares will be in effect from Trunk Line territory to Denver and return at the time of the above convention, of which your members can, if they so desire, avail themselves, and they can secure full information as to these fares by applying to the ticket agents of the several lines. For your information we might state that a fare of $86.75 will apply from Washington to Portland, Seattle, and other Northern Pacific Coast points and return, account of the Alaska-Yukon-Pacific Exposition; tickets to be sold from May 20th to September 29th, and to bear return limit of October 31st. Fare of $101.75 will apply from Washington to San Francisco and return, one way *via* Portland. * * * Tickets sold at the fares named permit of stop-over at Denver in either direction.

NEW ORDER IN REGARD TO RECOMMENDATIONS OF REFEREES.

The resolution adopted in 1908 necessitating the forwarding of the recommendations of referees to the chairmen of the appropriate subcommittees for consideration in

advance of the meeting is here repeated, and all referees are urged to comply therewith both to avoid confusion at the time of the meeting and to insure that the recommendations receive a more careful consideration than is possible otherwise:

Resolved further, That this committee shall organize from its membership three subcommittees, corresponding to the present committees A, B, and C, to whom all recommendations of new methods or of changes in methods, provisional or official, shall be submitted *not later than three weeks prior to the date of the meeting of the association* at which it is desired that the recommendations in question shall be considered, and said committee on recommendations shall report to the association, with its approval, disapproval, or suggestion of amendment, all recommendations submitted in due form for its consideration.

The chairmen of these committees, to whom the recommendations should be sent, in triplicate if possible, and the subjects pertaining to each committee, are as follows:

Committee A (nitrogen, potash, phosphoric acid, soils, ash, insecticides, and water).—Chairman, J. K. Haywood, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

Committee B (dairy products, foods and feeding stuffs, sugar, tannin, and medicinal plants and drugs).—Chairman, F. W. Woll, Agricultural Experiment Station, Madison, Wis.

Committee C (food adulteration, including separation of nitrogenous bodies).—Chairman, A. L. Winton, U. S. Food and Drug Inspection Laboratory, Manhattan Building, Chicago, Ill.

The return of the enclosed postal is requested.

H. W. WILEY,
Chief, Bureau of Chemistry,
Secretary, Association of Official Agricultural Chemists.

Washington, D. C., May 17, 1909.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, LONDON, MAY 27th to JUNE 2nd, 1909.

The Seventh International Congress of Applied Chemistry opened on May 27th with felicitations from the Prince of Wales which were responded to by representatives of several different countries in well-chosen words. The Prince showed a comprehensive grasp of the great objects of the Congress as the following quotation from his admirable address clearly indicates: "Applied chemistry means a great deal more than chemistry whether pure or technical. It requires knowledge of materials and their supply, knowledge of mechanics and engineering, a keen eye for sites and advantages of transit, careful utilization of by-products, knowledge of markets and finance, and various other things not taught in universities or technical schools."

With more than one thousand papers in the eleven sections of the Congress most of them had to be abbreviated—and many only read by title. It would seem better in this brief to call attention to some salient points in some interesting papers, knowing full well that many interesting papers cannot be even referred to. The many receptions and social functions lasting till midnight facilitated the meeting and acquaintance of the members, and too much credit cannot be given the English committees for the thorough accomplishment of their work for the five thousand in attendance.

Possibly no problem in industrial chemistry at the present time is more epoch-making than that of the oxidation of atmospheric nitrogen. There were three papers by Prof. Bernthsen, N. Caro and C. Weiss. The illustration of the electric arc about 24 inches long—using a glass tube by Prof. Bernthsen was exceedingly attractive and interesting. In the start from the bottom like a fountain of fire which was quickly continuous in the upward direction, the air being drawn in and following the regular flow of the arc and subjecting the nitrogen to continuous oxidative influences. The brown color of the oxides of N quickly appeared in the glass globes about 12 inches in diameter which were placed in the air circuit. The process is now working on the large scale in Norway where arcs eight yards long are in operation and provision is being made for an ultimate development of a million horse power for this manufacture. It is also understood that a like amount of power is desired in the United States for a similar development.

The address before the whole Congress by Prof. Dr. O. N. Witt was very brilliant, at the conclusion of which one American arose and said he had come four thousand miles to this Congress, and if he obtained no more than this address he considered himself well repaid for his expenditure of time and money. Dr. Witt indicated the grand desirability of a knowledge of the history of industrial processes in oriental countries and the islands of the seas, as some of them were vanishing before the tread of our now rapid and commercial methods. Vanishing not because their methods were ineffective but because they could not commercially compete—to quote as follows. "It is true that the scientific method of invention is a quicker road to success. Rapidity is everything in our times. Whirling along in a motor carriage to a well-known destination is distinctly more agreeable than tramping on foot in the glaring sun of the summer's day; but one cannot pick flowers blooming by the wayside or stumble over hidden treasure at the rate of sixty miles an hour. * * * In this struggle for existence the fittest means the cheapest and quickest."

The methods in Germany with chimneys and coal or gas-heated furnaces are quite distinct from the development that shall come to Norway and Sweden with electrical methods derived from the so-called "white coal" without chimneys, etc.

The description of the working of the Townsend cell by Dr. Baekeland revealed a solid and economical industry that is soon to use 4,000 kw. per 24 hours, and Mr. E. A. Sperry's account of the manufacture of liquid Cl and the detinning of sheet tin were of exceeding interest and commanded the earnest attention of all present.

In closing, I may say a start was made in this Congress on Conservation of Natural Resources and a place has been made for its definite consideration at the next Congress in 1912 in the United States, Dr. Edward W. Morley being made Honorary President and Dr. W. H. Nichols President of the next Congress.

EDWARD R. TAYLOR

ABSTRACTS FROM THE SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, LONDON, 1909.

The Legal Status of Industries Giving Rise to Noxious Gases; The Smelter Smoke Question in The United States

By Charles Baskerville, Ph.D., F.C.S., Professor of Chemistry and Director of the Laboratories, College of the City of New York.

This paper contains a review of the American laws regulating the pollution of the air with noxious or offensive gases, with a discussion of the cases in point of rule, general decisions, and the remedies proposed for the suppression of such nuisances.

It is shown that there is neither entire uniformity nor definiteness of statement in the codes of the several States, and that no specific regulations obtain. After a discussion of the foreign laws on the subject, the solution of the "smelter smoke question" is considered. It is pointed out that considerable progress has been made by some manufacturers toward the installation of waste-recovering devices, and that the enforced use of such contrivances by the enactment of a Federal law regulating the amounts of waste gases to be permitted to pass into the air will alone solve this great national industrial problem. However, the geographical and meteorological conditions prevailing in the various States must be carefully considered.

The paper is replete with legal citations.

On the Progress in the Application of Synthetic Indigo and its Derivatives in the Textile and Dyeing Industries.

By M. Liebert, Ph.D. (Meister Lucius & Brüning, Ltd.)

Synthetic indigo identical chemically and in its application with the natural product—Manufacture by sodium amide process in Ellesmere Port—Chemists and colorists study the reactions, explain the process of dyeing, and improve the application—Application based on reduction to indigo white. This is brought about by fermentation or by chemical ingredients—Wool dyeing: Drawback of the old bi-vats and advantages of the ammonia vat—Cotton dyeing: Advantages of hydrosulphite soda vat—Printing: Glucose process; direct printing with hydrosulphite formaldehyde; discharge printing—Various forms of indigo—Economic aspect brought about by the arrival of the synthetic product—Indigo halogen derivatives—Thioindigo red and its derivatives—Future of vat colors.

Electrolysis of Brine with Double Diaphragm and Percolating Electrolyte.

By R. H. F. Finlay and F. G. Donnan.

The paper gives a short account of experiments made to test the electrochemical efficiency of a type of electrolytic cell, designed by Messrs. A. and R. H. F. Finlay, for the technical electrolysis of saturated brine solutions (production of caustic soda and chlorine). The cell is characterized by containing two diaphragms and three compartments, anodic, middle, and cathodic. The electrolyte solution is fed into the middle compartment, and flows continuously under a slight pressure-head through the anode and cathode diaphragms into the anode and cathode compartments, and continuously leaves these by suitable (adjustable) swan-neck outlet tubes. The counter-flow of the electrolyte greatly aids in diminishing the migration of the hydroxyl ions from the cathodic to the anodic compartments, and in preventing diffusion or convection of dissolved chlorine in the opposite direction. In order to reduce resistance the various compartments are simply thin sheets of liquid a few millimeters thick, and these can be built up and bolted together in any number, somewhat after the fashion of a filter-press. The inflow and outflow of liquids and gases are provided for by a simple system of corresponding slots and holes cut in the diaphragms, electrode frames, and separators. Experiments made with Bernfeld asbestos diaphragms 2–3 mm. thick have shown that the best working conditions of the cell are as follows:

Electrolyte.—Saturated brine at ordinary temperatures.

Current Density.—About 0.02 amp. per sq. cm. of diaphragm section.

Concentration of Caustic Soda Produced.—Eight grams per 100 cc. of cathode effluent.

Cathode Current Efficiency.—96–8 per cent.

Cell Voltage.—3 volts.

Thermic Reaction in Vacuo.

By Frank E. Weston, B.Sc., and H. Russell Ellis, B.Sc.

Since the commercial development of the Goldschmidt reaction, namely, the reduction of Fe_2O_3 by Al, *i. e.*, the "Thermite Reaction," many reactions of a similar nature have been studied, such as the action of Al upon nearly all the oxides with the production of metals and alloys, the reduction of B_2O_3 and SiO_2 by Al (Weston and Ellis), reduction of oxides and sulphides by Ca and of CaO by CaH_2 (F. M. Perkin), the action of Mg, Ca and Al upon MgO, Al_2O_3 and CaO (Weston and Ellis), action of calcium alloys upon certain oxides, reduction of oxides by Si and B, etc., etc. These reactions are all accompanied with a great evolution of heat, and they are all similar in one very important respect, namely, they require a certain amount of heat energy to be imparted before reaction proceeds. The initial energy can be supplied.

(1) Lighted match or taper starts reaction between Al and Na_2O_2, Mg and Na_2O_2, etc.

(2) Heat generated by such mixtures as Al and Na_2O_2 or by a piece of burning Mg ribbon starts many reactions, such as Al_2 and Fe_2O_3, B_2O_3 and Al_2, etc.

(3) Many mixtures require initially heating throughout the whole mass and then react with a fuse, such as 2Al + 3CaO, $3SiO_2$ and 4Al.

(4) Mixture heated before reaction and external heat supplied during the reaction.

In studying such thermic reactions the cause is not always evident, and the reaction is not always so simple as in the case of the thermic reaction, *i. e.*, the simple transfer of the oxygen.

In many reactions the presence of air has a very great influence over the course of the reaction and on the nature of the products; many reactions can be arrested by the exclusion of air and re-started by exposure to air. An initial high temperature is required to start all thermic reactions, and when two oxides are being studied the heats of formation of which are close external heat must be sup-

plied to change the oxygen from one metal to the other. This heat can be obtained from an external source or from the combustion of the reducing agent with the oxygen or nitrogen of the air or both.

In the interaction of Al powder and carbon, a very large amount of nitride is produced with smaller amounts of carbide (Weston and Ellis), and on the reduction of BaO, SiO, and CaO by Mg large amounts of nitrides are also formed, similarly with many other reactions.

The authors explain the formation of Al_4C_3 from mixtures of Al and C as follows: "Air plays a most important part, the first action being the oxidation of C to CO and CO_2, producing sufficient heat to cause the oxidation of Al to Al_2O_3, and this latter reaction raising the temperature sufficiently high to cause the combination of the Al with the C, as well as the Al with the N, the N coming both from the atmosphere and the occluded gases." *Trans. Far. Soc.*, Vol. IV., p. 60. With a view to ascertaining what part the atmosphere plays attempts have been made to carry out such reactions *in vacuo*. Very few workers have put experiments of such a nature on record. In their experiments the authors of the present paper met with difficulties in starting such reactions when air was excluded, the various reactions taking place with vigor when air was present.

The various mixtures were heated *in vacuo* by glowing platinum wires up to the melting point of platinum, by iron wires and by igniting a fuse of $4Al + 3Na_2O_2$, but very few reactions took place, and many which started only continued for a short while.

The reactions between Al_2 and Fe_2O_3, $4Al + 3Na_2O_2$, $2Mg + Na_2O_2$, $Mg + Na_2O_2$, $3Mg + Na_2O_2$, $Al_2O_3 + 3Mg$, $Mg + SiO_2$, $2Mg + SiO_2$ have all been brought about *in vacuo*, but always more quietly than in the open air and with different products. A very large number of other mixtures have been tried, but up to the present without success, the difficulty being to produce a great initial "heat density" without which, air being excluded, action will not take place. The work is being continued, and the various mixtures heated before firing the fuse, etc.

The authors would particularly point out that the contribution to the subject of "Thermic Reactions" is put forward in this incomplete form in the hope that it may lead to a discussion of this highly interesting type of reaction.

Calcium-Carbide.

By C. A. Hansen.

The equilibrium CO pressure in the reaction between CaO and C was determined at 1,380°, 1,530°, and 1,780° C. by sealing the reagents in an evacuated furnace which could be kept at constant temperature and measuring the CO pressure on a mercury manometer. The extrapolated pressure-temperature diagram indicates reaction at a temperature as low as 1,275° C.

It was shown that at 1,450° reaction took place when the CO pressure was kept below its critical value, and that at the same temperature, in a sealed furnace, reaction ceased when the critical pressure was established.

In the paper is a short list of reduction temperatures for various oxides + carbons, determined in the same furnace as given.

Relative Efficiency of the Arc and Resistance Furnace for the Manufacture of Calcium Carbide.

By Samuel A. Tucker.

Calcium carbide was prepared in the two types of furnace mentioned under conditions which would give the best yield. Comparison is made of the product as to its carbide content and its weight obtained per energy unit.

The results show that for the scale on which the experiments were conducted that the resistance furnace is much superior to the arc.

The best results obtained with the arc furnace was 1,170 watt hours per 100 grams of pure carbide, while with the resistance furnace the same quantity of pure carbide was obtained with 544 watt hours.

Information is also given as to the best proportions of lime and coke to be used with the two types of electric furnaces employed.

On Jaffé's Colorimetric Method for the Estimation of Creatinine.

By A. Chaston Chapman.

The author has shown that the red coloration on which this method is based depends, not on the formation of creatinine picrate, but is due to the reduction of the picric acid in alkaline solution to a mixture of amido-dinitrophenol (picramic acid) and diamido-nitrophenol, the alkaline salts of which are deeply colored. The same coloration is produced by numerous reducing agents, such as nascent hydrogen, hydroxylamine, acetone, aldehyde, ammonium sulphide, and titanium trichloride. Creatinine acts as a powerful reducing agent, and if it is present in excess the picric acid may undergo reduction to colorless triamidophenol. Color measurements showed the red coloration to be due to both the monamido and the diamido-phenol, and that solutions of the sodium salt of picramic acid could not be used for matching purposes. Since the coloration is due to a somewhat complex reducing action, it is clear that the conditions under which the test is carried out must be fairly closely defined if accurate results are to be obtained.

Influence of Temperature.—This factor is of considerable importance, since up to a certain point the color is increased, after which there is a reduction due to the formation of triamido-phenol.

Influence of Time.—This factor is of much less importance than the preceding, and slight differences have no appreciable influence on the results. The general effect is, however, of the same character as in the case of the temperature factor—that is to say, there is at first an increase and then a reduction of the color intensity.

Influence of the Presence of Dextrose.—As in certain commercial products, dextrose and creatinine may occur together, experiments were made to ascertain whether the former substance exerted any influence on the estimation of the latter. It was found that in the cold, and under the ordinary conditions of the test, dextrose was without appreciable effect.

In conclusion, attention is called to the necessity of working in sufficiently dilute solutions, in analyzing highly colored products, since the disturbing effect of the color may be very considerable.

Contributions from the Laboratories of the General Chemical Company of New York.

I.—The Determination of Small Amounts of Arsenic by the Gutzeit Method.

A detailed description, with diagram, of an improved apparatus and method for use in the determination of small amounts of arsenic by the Gutzeit method. The test paper used is sensitized with a 0.5 per cent. $HgCl_2$ solution. The standard stains are made from a standard *arsenate* solution, coated with paraffin and sealed in a glass vessel over P_2O_5 to prevent deterioration. Development of the stains with NH_4OH or HCl is unnecessary.

II.—The Determination of Minute Quantities of Arsenic in Brimstone.

Brimstone is oxidized by a mixture of three volumes of carbon tetrachloride to two volumes of pure bromine, followed by nitric acid. A little water is added and the nitric acid and carbon tetrachloride removed by evaporation. Arsenic is then determined in residue by Marsh or Gutzeit method.

III.—The Determination of Arsenic in Sulphuric Acid.

Arsenic, when more than 0.002 per cent. is present in concentrated sulphuric acid, is reduced by tartaric acid. The excess of the latter is removed by heating, and the As_2O_3 titrated with standard iodine solution, after neutralization with ammonia and bicarbonate of soda.

IV.—The Volumetric Determination of Sulphur in Pyrites Cinders.

Sulphur is oxidized by heating the cinders with a mixture of one part sodium carbonate and four parts zinc oxide with access of air, the resulting sulphate extracted with water and titrated with standard barium chloride solution in the presence of alcohol, excess being added and titrated back with sodium carbonate solution. Method is rapid.

V.—The Determination of SO_2 in Dry Gases.

Orsat apparatus made available for the purpose by use of chromic acid in concentrated phosphoric or sulphuric acid solution.

VI.—Note upon Marsh or Gutzeit Tests.

Presence of impurities such as lead in the zinc used for the Marsh or Gutzeit test sometimes causes suspension of hydrogen evolution. Addition of a colloid to the acid solution counteracts this and facilitates even evolution of hydrogen.

VII.—The Electrotitrimeter.

Description of means and method of determining percentage concentration of acids, alkalies and salts in solution, based upon measuring their electrical resistance in comparison with a like solution of known strength. The difference of electric conductivity between the standard and the material under examination is observed by means of a device similar to a Wheatstone bridge. The effect of variations in temperature is avoided by keeping the contents of both the standard and the testing tube under the same conditions.

The Lash Steel Process.

By Francis A. J. Fitzgerald.

The Lash steel process was worked out as a result of several years of experimenting by Mr. Horace W. Lash on the direct production of steel from iron ore. These experiments showed that by using a mixture of iron ore, coke fluxes and granulated pig iron or cast iron borings, a commercially feasible process might be carried on. The Lash mixture has, approximately, the following composition:

Granulated pig iron	23 per cent
Ore	60 " "
Coke	11 " "
Lime	6 " "

Several hundreds of tons of steel have been manufactured by this process in the open-hearth furnace, and this has shown that: (1) A superior quality of steel is obtained; (2) The cost of production is in general lower than when the regular methods are employed. Experiments have also been carried on in the electric furnace, using the Lash process. Fifty tons of steel were made in this way. Tables are shown for the purpose of comparing regular steel-making practice with the use of the Lash process in the open-hearth and electric furnaces.

Observations on the Absorption by Iron of Carbon from Carbon Monoxide.

By Charles F. Burgess and James Aston

Doubly-refined electrolytic iron, containing 0.012 per cent. carbon or less, was placed in magnesium oxide crucibles and these in graphite crucibles, which latter were embedded in an electric resister furnace, the resister material being granulated carbon. When the iron is melted, two to three hours are required to attain a maximum temperature of 1,800° C., and a period of six hours more elapses before the iron has cooled to 600° C.

A 500 gram ingot, after melting, shows a carbon content of 0.047 per cent., and one of 2,000 grams 0.012 per cent. After forging, the carbon contents were 0.047 per cent. and 0.028 per cent. respectively, showing that there is comparatively little absorption of carbon in the rapid heating of the iron in the forge fire, preparatory to forging. When lime was added with the iron in the magnesia crucible there was an increase in the carbon absorption, which rose to over 0.2 per cent. when metallic calcium was introduced.

Molybdenum, tungsten, chromium and silicon apparently have a marked influence upon the carbon absorption, while tin, silver, arsenic and cobalt have less influence.

The carbon comes from the reaction

$$Fe + CO \rightleftarrows FeO + C.$$

The carbon which is set free above 800° is taken up by the iron by cementation.

Regarding the Question of the International Regulation of the Potash Factor.

By Prof. Precht, Neu Stassfurt.

For its quantitative determination, potash was formerly precipitated exclusively by means of platinic chloride solution as potassium platinic chloride, and weighed after washing and drying. The potash content was then calculated from the weight of the precipitate on the basis of the atomic weight of platinum as 197.18. The results of the investigation made by Seubert about thirty years ago, however, showed that the old determination of the atomic weight of platinum was not correct and that the real atomic weight was 195. Consequently, at a meeting held on the 9th of August, 1892, in the Potash Syndicate for the purpose of discussing the uniform methods of analysis in the potash industry the

question was raised, What atomic figure should be taken as a basis for the determination of potash? At these negotiations the committee of the potash mines was represented by Messrs. Oberbergrat Schreiber and Kommerzieurat Dr. Borsche, while the syndicate was represented by Messrs. Director Georg, Dr. Tietjens and Lierke. Moreover, twelve representatives of the potash mines under the syndicate and of the chemical factories belonging to them took part in the discussions.

As a result of these discussions it was decided to retain the old atomic weight of platinum, *viz.* 197.18, and to adopt as factors for the calculation of the amounts of muriate of potash, sulphate of potash and pure potash from the potassium platinic chloride found the figures 0.3056 for KCl, 0.357 for K_2SO_4, and 0.1928 for K_2O. The reason for retaining the old atomic weight was that in the actual determination of potash chemically pure potassium platinic chloride is never weighed but that the result is generally too high on account of filth and a small water content. In order to balance this error, the correct atomic weight, *viz.* 195, found as the result of the new investigation, and which, of course, would give a higher result, was not taken as a basis for calculation, but the old atomic weight, which is no longer recognized as being correct.

As is known, it is necessary in the analysis of sulphate of potash to precipitate the sulphuric acid by means of barium chloride. In this process some potash is brought down in an insoluble form by the barium sulphate precipitate so that the result of the potash determination falls too low. It was therefore decided at that time to add 0.3 per cent. K_2SO_4, as a correction for the above error in the analysis of sulphate of potash.

The resolutions adopted at this meeting of the 9th of August, 1892, on which there lies before you a printed report, still retain their validity in the methods of analysis employed at present in the potash industry.

Besides the platinic chloride method, which was regarded at that time as the only authoritative one, the determination of potash by means of potassium perchlorate came to be adopted later more and more generally. At the International Congress of Applied Chemistry held in Berlin in 1903 I brought forward the advantages of the potassium perchlorate method at a common meeting of the Section for Agricultural Chemistry and the Section for Analytical Chemistry, and consequently it passed into general practice and was introduced by most of the agricultural experiment stations. In the case of the potassium perchlorate method, the question of the international regulation of the potash factor disappears, as we have no longer to deal with the atomic weight of platinum, but with the exactly determined atomic weights of potassium, chlorine and oxygen. Moreover, the potassium perchlorate is absolutely pure and easy to dry, so that there is no source of error with the potassium perchlorate as with the platinum method. The international regulation of the potash factor is, therefore, only important when it is desired to check the now generally employed potassium perchlorate method by the older platinic chloride method, for example, in the case of a disputed analysis. Such check analyses should be but seldom necessary, as the potassium perchlorate method has been so carefully elaborated that an exact and reliable result can be guaranteed if strict adherence be kept to the various rules.

The Potash Syndicate itself has no reason for changing the rules connected with the methods of analysis, as it has been found by experience that correct results are obtained by working in accordance with the present rules. If, however, the International Commission for the analyses of artificial manures and feeding stuffs is determined to fix internationally the potash factor in the case of the determination of potash by means of platinic chloride, I am of the opinion that the old rule, which cannot be kept for ever, should be allowed to drop and that the newer accurately and scientifically determined atomic weight 195.0 of the International Table of Atomic Weights of 1909 should be adopted. The factor for muriate of potash would then be, not 0.3056, but 0.30686, and the results of the potash determination consequently higher than before. At the same time, however, a correction in the form of a deduction from the result found would have to be made as a precaution against complaints on the part of purchasers that they are being duped by too high analytical results. For high percentage muriate of potash the correction would be 0.3–0.4 per cent. In the analysis of sulphate of potash such a deduction would not be necessary; we would require merely to neglect the usual enhancement of the result by 0.3 per cent.

In the analysis of low percentage manure salts or crude potash salts there is only a very small correction to be made, and it would be expedient to determine this again by numerous tests, as the platinic chloride method will be employed in the future only in the case of check analyses, and consequently I prefer to leave the question undecided whether or how high the correction should be made in the analysis of crude potash salts if pure platinic chloride be used.

The foregoing remarks might be summarized as follows: In an international regulation of the potash factor the proper atomic weight of platinum, 195.0, should be adopted, and those corrections prescribed which are necessary for obtaining as accurate results as possible with the different brands. For sulphate of potash the correction at present used would be allowed to drop.

PERSONAL NOTES.

Mr. J. H. Linton, of the Vilter Mfg. Co., of Milwaukee, and Mr. A. W. Gregg, of the Bucyrus Co., of South Milwaukee, have formed a partnership to be known as The Pacific Coast Testing Laboratories, with headquarters in Seattle.

At the May meeting of the Utah Society of Engineers, held on the 21st of the month, Mr. Edward Fink gave a paper upon the Fink smelter and the experiments that have been carried out with it thus far.

The Seniors of the Colorado School of Mines, under the direction of Dr. Traphagen and others, made a trip of inspection through Colorado, Utah and Montana mining and smelting centers.

Seniors of the Utah State School of Mines are making a three weeks' tour of Wyoming, Colorado, Texas, Arizona,

California and Nevada. Professors Bradford and Overstrom are in charge of the party.

The business of the Arthur D. Little Laboratory of Boston, established in 1886, has been incorporated under the name Arthur D. Little, Inc., in order that the facilities of the laboratory may be further extended and to secure permanency in its organization. The company is prepared, through its large staff of specialists, to undertake any work involving the application of chemistry to industry.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, 908 G. Street, N. W., Washington, D. C.

912,298. Process of Melting Pig-iron and Steel. HOLDEN A. EVANS, U. S. Navy. February 16, 1909.

This is a process of melting iron, or steel in an oil- or gas-fed furnace by producing a suitable flame; regulating the same to cause its hottest part to play on the metal while its oxidizing part plays above the same; in collecting the molten metal; and in causing the cooler part of the flame to maintain the said metal in its molten condition.

912,509. Process of Manufacturing Gas. BERNHARD THIEMICH, Dresden-Nausslitz, Germany. February 16, 1909.

This is a process of producing gas from pulverized coal for actuating internal combustion engines by causing the coal to fall intermittently in measured quantities on to a surface, heating said surface by the exploded gases of the engine, pressing it against this furnace, and removing the residue after the separation of the gas, before a fresh charge of coal is supplied, and delivering the gas to the engine.

912,540. Pyritic Smelting. JAMES T. CARRICK, Johannesburg, Transvaal. February 16, 1909.

This process consists in producing in the furnace at the base of the focus region of slag formation, a restricted zone having a temperature higher than that of the rest of the furnace by injecting combustible at that point and effecting its combustion within the furnace.

912,568. Method of Roasting Ores. HENRY K. HESS, Philadelphia, Pa. February 16, 1909.

This method of roasting ores consists in providing a series of circular portable pots of heat-resisting material, placing the ore in said pots and arranging the pots in horizontal tiers, one upon the other within a heating chamber and heating the ore-containing pots in said chamber.

912. Manufacture of Hydrated Sodium Carbonate. WILLIAM E. RIDENOUR, Philadelphia, Pa. February 16, 1909.

The process consists in intimately mixing definite proportions of water and sodium carbonate without dissolving the sodium carbonate, the water used being limited to an amount insufficient to effect the crystallization of the produce.

912,744. Process of Recovering Sulfur from Sulfur-bearing Gases. PAUL S. SMITH, Wilmington, Del. February 16, 1909.

This is a process of recovering sulfur from sulfur dioxid by alternately manufacturing water-gas and producer gas in each of a plurality of separate generators, and simultaneously manufacturing water gas in one generator and producer gas in another, leading the water-gas formed successively in the several generators and sulfur dioxid to a common point, and successively utilizing the producer-gas formed in the several generators to produce the heat required for the reaction of the mixed gases.

913,275. Process of Detinning. HENRY M. FERNBERGER, Dollar Bay, Mich., and WILLIAM W. MURRAY, Philadelphia, Pa. February 23, 1909.

In this process the tinned metal is subjected to the action of anhydrous carbon tetrachlorid, containing dissolved chlorin

914,100. Electrolytic Process of Producing Compounds. CHARLES E. ACKER, Niagara Falls, N. Y. March 2, 1909.

The process has particular reference to producing cyanogen compounds, by continuously electrolyzing a molten compound of a metal, alloying the separated metal with a cathode metal, removing the alloy and reacting on the alloyed metal with nitrogenous and carbonaceous reagents, and returning the residual metal to the cathode.

914,113. Gunpowder. CONRAD P. H. CLAESSEN, Berlin, Germany. March 2, 1909.

The explosive consists of an intimate mixture of nitrocellulose, nitroglycerin, vaseline and potassium lactate.

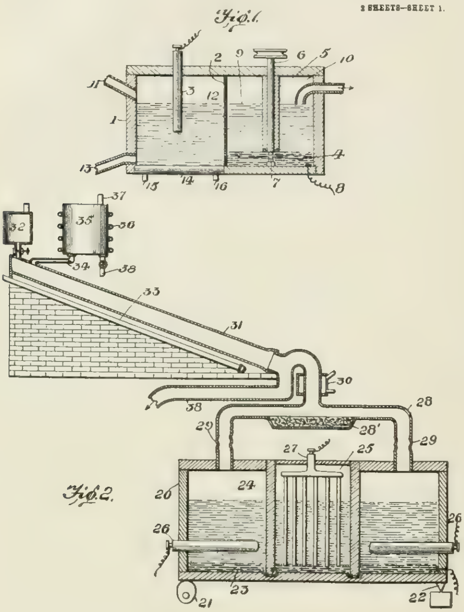
914,187. Process of Manufacturing Aluminum Compounds. ERIK L. RINMAN, Gottenbert, Sweden. March 2, 1909.

The process consists in directly heating a mixture of alumina-containing materials with ammonium salt, to the temperature of reaction of said ammonium salt, generating ammonia and forming the aluminum salt of the corresponding acid of the ammonium salt.

914,251. Process of Chlorinating Organic Bodies. CARLETON ELLIS, White Plains, N. Y., and K. P. MCELROY, Washington, D. C.

This method consists in electrolyzing a suitable chlorid and leading or bringing the evolved chlorin into direct contact with the hydrocarbon to be chlorinated. The hydrocarbon to be chlorinated may be placed directly in the anode chamber, either as such on in solution in a suitable indifferent body, such as chloroform, tetrachlorid of carbon or one of the oily carbonated bodies formed by the present method. As a rule however, and especially in the case of naphthalene and anthracene, the inventor prefers to conduct the whole chlorination with the hydrocarbon in the vaporized condition and contained in a chamber, this permitting more exact control of temperature, admixture and amount of the reacting bodies and other conditions of vital importance in obtaining specific products. This chlorinating chamber is provided with temperature controlling means, and for many chlorinations is perferably at least partly of glass to permit illumination. The inventors state that actinic

light is often useful in facilitating the reaction. They have discovered that the presence of an inorganic catalyzer is often of importance in facilitating a reaction. Such substances as iron oxid, pumic stone, bone-black, charcoal or copper oxid are useful for this purpose. The use of electrolytic chlorin in a temperature-controlled lighted tube



or chamber and in the presence of these inorganic catalyzers, is advantageous for making chlorin derivatives of many organic bodies besides the polyring hydrocarbons hereinbefore specified, as for instance in chlorinating paraffin hydrocarbons, in forming chlorin derivatives of acids, etc.

The illustration shows a form of apparatus in which the process may be advantageously carried out (Figure 2). Carbid is heated in proximity to commingled vapors of substances containing carbon and silicon to a temperature sufficient to cause the carbon and silicon to combine throughout the pores of the silicon carbid mass.

914,279. **Process of Obtaining Nitrogen from Air.** Oliver P. Hurford, Chicago, Ill. March 2, 1909.

The process consists in first burning a carbonaceous fuel in the presence of air of sufficient quantity for complete combustion to carbon dioxid and substantially free from carbon monoxid, then subjecting the gaseous products to the condensing action of water to condense the steam and separate the carbon dioxid from the nitrogen and then leading off the nitrogen from the condensing chamber.

913,430. **Method of Precipitating Metals Electrolytically.** Arthur Ramen, Helsingborg, Sweden. February 23, 1909.

The process consists in reducing a solution containing reducible metals by means of metallic iron, electrolyzing a solution containing readily electrolyzable metals and maintaining a body of such reduced solution about the anode during such electrolysis.

913,535. **Metallurgical Process.** George Moore, New York, N. Y. February 23, 1909.

This is a process of separating metals from their ores by volatilizing salts of the metal in a suitable vessel, forcing steam upwardly through the subjected ores, and condensing the impregnated steam.

913,606. **Boiler Compound.** Harry R. Young, Catasauqua, Pa. February 23, 1909.

The boiler compound comprises about 80 per cent. of powdered soapstone, about 18 per cent. carbonate of soda, and about 2 per cent. brown sugar.

913,653. **Process of Manufacturing Nitroglycerin.** Franz Aigner, Potsdam, Germany. February 23, 1909.

The process consists in nitrating a quantity of glycerin with a suitable quantity of a fresh mixture of concentrated nitric and sulfuric acids, separating the resultant tri-nitroglycerin from the partially exhausted acids, containing less highly nitrated derivatives of glycerin, adding a suitable quantity of fresh concentrated nitric and sulfuric acids to restore the acid mixture to substantially its original percentage content of nitric acid, sulfuric acid and water, and nitrating a second portion of glycerin with said acid mixture.

913,657. **Solution for Treatment of Iron or Steel.** Albert Hayes, New York, N. Y. February 23, 1909.

The solution comprises chlorid of ammonium and hippuric acid.

913,679. **Wood-pulp and Process for Making Same.** Carl Bache-Wug, Berlin, N. H. March 2, 1909.

The pulp is composed of untreated fibers mixed with fibers treated with a solution of sodium chlorid and containing substantially all the lignin which is originally contained in the wood from which both fibers are obtained.

913,708. **Process of Separating Metals in Solution.** Herbert H. Dow, Midland, Mich., and Walter S. Gates, Worthington, Ontario, Can. March 2, 1909.

The process consists in adding to the solution a reagent capable of producing a relatively insoluble precipitate with one of the metals, such reagent being added in an amount equal to the chemical equivalent of said one metal; and then agitating the resultant mixture until any inclusions of the other metals are substantially dissolved out.

913,713. **Artificial Fuel.** Alexander H. Ege, Mechanicsburg, Pa. March 2, 1909.

The fuel embodies alcohol, coal dust, starch paste, petroleum, common clay and cement.

913,758. **Process of Making Sugar.** George W. McMullen, Chicago, Ill. March 2, 1909.

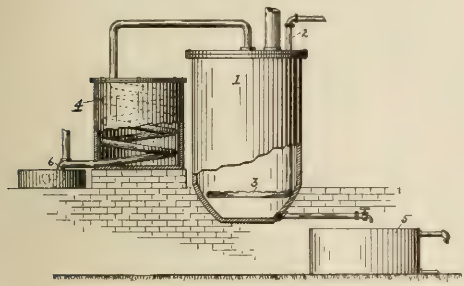
The process consists in cutting the sugar-producing plant into slices, desiccating the cut material into a brittle condition, comminuting the desiccated material, saturating the material and finally separating the saccharine liquid from the solids and recovering the sugar therefrom.

913,762. Process of Manufacturing Baking-powder. RICHARD PAUL, Berlin, Germany. March 2, 1909.

This powder is made by mixing tartaric acid with froth-forming albumen, beating the mixture to froth, drying the mixture beaten to froth and mixing it with bicarbonate of sodium.

913,780. Producing Benzene or Its Homologues from Petroleum. ERIC A. STARKE, Berkeley, Calif. March 2, 1909.

This process is only applicable to those petroleums, the distillates of which contain the benzene nucleus, by which is meant petroleum which contains hydrocarbons having benzene or its homologues, either free or in some form of combination, such for example as "California" or "Japanese" petroleum. Though these combinations have, as yet, not been accurately determined, certain hydrogenized homologues of benzene as for example di-hydro-toluol, di-hydroxylene, and others have been recognized; and besides these forms, benzene or its homologues exist in the free state in some oils. The inventor has found that if the distillates of these petroleums which contain the benzene nucleus, either free or in some form of combination, are acted upon



by sulfuric acid, with the aid of heat, oxidation takes place, resulting in the formation of sulfonic acid and sulfuric dioxid. This is taken advantage of in this process, which consists in mixing a distillate of petroleum which contains a benzene nucleus, with concentrated sulfuric acid; then heating the mixture during agitation until the evolution of sulfur dioxid has about ceased; then allowing the mass to settle until the sulfonic acids have separated from the petroleum; and then recovering the benzene from this sulfonic acids by distillation. The illustration shows the apparatus in which the process is carried out (see figure).

913,794. Process for Making Cement. EDWARD J. WINSLOW, Chicago, Ill. March 2, 1909.

This is a process of preparing a relatively water-proof cement by dry grinding cementitious material with a relatively small quantity of a suitable water-proofing agent.

913,887. Process of Preparing Carbid of Calcium. XAVIER HERME, Fruitvale, Calif. March 2, 1909.

The process consists in placing the following substances in a receptacle in the order mentioned; namely, sugar, carbid, a refined oily substance, sugar glucose in liquid form heated to the boiling point, agitating the substances so placed, and thereupon placing an additional amount of sugar in said receptacle and continuing said agitation.

914,343. Process of Making Storage-battery Electrodes. THOMAS A. EDISON, Llewellyn Park, Orange, N. J. March 2, 1909.

The process consists in coating granular material with conducting metallic films or scales, in compressing the mass to secure coherence thereof, and in subjecting the scales or films to a welding temperature.

914,382. Composition for Tanning. IRA I. BURROWS, Poolville, Tex. March 9, 1909.

The composition contains water, fluid extract of phytolacca, or common poke root, gum gambier, and alum.

914,523. Compound Fuel. ABRAHAM D. SHEPARD, San Francisco, Calif. March 9, 1909.

The fuel is in the form of briquets consisting of a mixture of normally non-briquetable coal and a low-grade briquetable coal containing an inherent binder which is liberated by pressure to unite the two coals.

914,624. Explosive Mixture for Combustion Engines. PAUL WINAND, Cologne, Germany. March 9, 1909.

The mixture consists of a suitable diluent, and two nitrated carbon compounds, which are separately non-explosive, but which are explosive when mixed.

914,633. Steel. HENRY D. BOOTH, Philadelphia, Pa. March 9, 1909.

The steel contains a small amount of copper and vanadium.

914,649. Process of Preparing Red Oxid of Iron and Zinc Sulfate. GEORGE EVANS, Stroud Green, England. March 9, 1909.

The process consists in treating low-grade zinc ores containing iron by treating the ore with sulfuric acid of about 50° Baumé to convert the sulfatizable metals into sulfates, calcining the mixture to decompose the sulfates of iron present, and drive off the sulfur, leaching out the zinc present, and separating from the mixture the residue of ferric oxid.

914,813. Process of Producing Nitric Oxids and Nitric Acid. OTTO DIEFFENBACH and WILHELM MOLDENHAUER, Darmstadt, Germany. March 9, 1909.

The process consists in passing over suitable catalysts a mixture of hydrocyanic acid and a gas containing oxygen at a temperature from 300° to about 600° C.

914,887. Process for Purifying Water. CARL W. SCHULTZ, Buffalo, N. Y. March 9, 1909.

The process consists in adding sulfate of aluminum, kaolin and starch to water and filtering.

914,916. Wire and Metal Cleaning Bath. JAY C. BENEKER, Pueblo, Colo. March 9, 1909.

This is a process of cleaning or picking iron or steel products, by subjecting the same to the action of a solution of acid containing a small amount of arsenious oxid.

915,029. Process of Detinning. FRANZ VON KUGELGEN and GEO. O. SEWARD, Holcombs Rock, Va. March 19, 1909.

In this process tin scrap is treated in a closed vessel with dry chlorin to form stannic chlorid, the temperature being

sufficiently high to effect complete detinning below that at which the iron is attacked.

915,401. Process of Purifying Rosin. HOMER T. YARYAN, Toledo, Ohio. March 16, 1909.

The process consists in treating with sulfuric acid a solution of rosin in a hydrocarbon solvent.

915,633. Sodium Sulfid. EMERSON H. STRICKLER, White Plains, N. Y. March 16, 1909.

This composition is a new form of sodium sulfid in the form of flakes or laminae of great purity and solubility, the laminae being of homogeneous composition and containing a high percentage of Na_2S, with a smaller amount of water than required for the crystallization of Na_2S.

915,774. Composition of Matter for and Process of Making Insulating Material. CARL A. KELLER and BERTRAND G. JAMESON, Chicago, Ill. March 23, 1909.

This composition is produced by mixing cement, sand, a water-proofing compound and water, molding the mixture, solidifying the molded form, evaporating the water therefrom, heating the form, and impregnating it while heated with an insulating fluid.

915,946. Process of Making Aldehydes. CARLETON ELLIS, White Plains, N. Y., and KARL P. MCELROY, Washington, D. C. March 23, 1909.

The process is produced by decomposing a formate by a low and regulated heat and removing the formaldehyde from the point of formation to a cooler point as fast as formed.

916,302. Method of Treating Metals, such as Steel or Steel Alloys. CHARLES J. GRIST, London, England. March 23, 1909.

The treatment consists in passing an electric current through the metal while the same is heated to a recalescent point in the presence of mercury.

916,449. Process for Recovering Waste Lime. JOHN G. JONES, Carthage, N. Y. March 30, 1909.

This is a process of purifying and revivifying spent or waste lime by reducing the same to a solid form, afterward drying the carbonate of lime in a solid form, and coarsely granulating the lime and reducing it by heat to an oxid state.

916,558. Process of Treating Glucose. HENRY A. HUGHES, Philadelphia, Pa. March 30, 1909.

The process consists in treating saccharine solutions for the purpose of eliminating the effect of sulfites and sulfurous acid residues present therein by determining the quantity of sulfites and acid residues in such solutions, and then adding an aldehyde of one of the primary alcohols sufficient in quantity to combine with said sulfites and acid residues and form a different and innocuous compound.

916,793. Production of Silicon. GEORGE O. SEWARD, East Orange, N. J., and FRANZ VON KUGELGEN, Holcombs Rock, Va. March 30, 1909.

In this process silicon is produced by subjecting a suitable silicon compound and a reducing agent to sufficient heat to reduce said compound and volatilize the silicon, while maintaining around or above the zone of reduction a cooler zone containing a non-oxidizing atmosphere in which the volatilized silicon is condensed.

916,900. Process for Electrolytically Producing Peroxid of Hydrogen. GUSTAV TEICHNER, Nuremberg, Germany. March 30, 1909.

INDUSTRIAL AND TRADE NOTES.

Acetone in France.—In reply to an inquiry relative to a report on the manufacture of acetone in Great Britain and France published in *Daily Consular and Trade Reports*, January 15, 1909, Consul Maxwell Blake, of Dunfermline, Scotland, forwards the following description of the method of making acetone in France, as ascertained from a British semiofficial report of the process:

The raw material used in the manufacture of acetone is wood, cut to meter (meter = 39.37 inches) lengths and varying from 1 to 8 inches in diameter. The kinds of wood used are elm, poplar, beech, and oak, which are common in underwood growths all over Great Britain. The sticks of wood are first carefully packed in retorts, which are hoisted by hydraulic cranes into the furnaces, the retorts being about 10 feet high by 5 feet diameter.

The iron retorts in which the wood is roasted are oblong in shape, and fitted with iron rings on each side for the purpose of the crane and an orifice at the top to allow the gases to pass out through the rest of the plant. The connections are plugged with clay when the retort is inserted in the furnace.

One of the admirable points about this system of Pages, Camus & Co. is that the tar produced from the wood is used as the fuel to create the heat necessary for the distillation. This wood tar is sprayed with a jet of steam and used much as oil is used in furnaces constructed for that particular fuel. In consequence the firm does not use any coal whatever in the process, which is in itself a great advantage; and if the industry in its new phase ever becomes a British one, the woodland areas and not the coal areas will be the place where the manufacture will most probably be established. It takes about 40 tons of wood to make a ton of acetone.

After the retort full of wood becomes sufficiently hot, the gases from the wood rise and fall through several continuous closed chambers, two of which are constructed with baffle plates in order that the wood tars may be caught and arrested early in the process. Eventually, at the end of the last closed chamber, the water, which has taken its proper share in the condensation of the vapors, comes out a black and oily compound. The result obtained is ordinary wood spirit, methylene acetone, and acetic acid. Methylene as usually employed for excise purposes is also obtained.

When the gases have been thoroughly expelled from the wood, only charcoal remains, which is used or sold. The annual production of this particular factory is as follows: Charcoal, 5,000 tons; tar, 1,000 tons; crude pyroligneous acid, 10,500 tons; methylene for excise purposes, 350,000 liters, or about 70,000 gallons.

As compared with former processes, the number of operations in this new method are fewer and more simple. There is also greater economy, few copper vessels being needed,

and there is the great advantage also arising from the use of the crude wood tar, which is one of the most difficult by-products to dispose of when not utilized for fuel. It is a curious fact, moreover, that the production of tar during the process seems to balance exactly the needs of the furnaces in which they are suspended and heated.

A summary of the chief features of the new process is as follows: (1) The utilization of the vapors arising from the stills containing the wood for the removal of a large proportion of the water distilled therefrom and consequent concentration of the resulting pyroligneous liquors; (2) the method of saturation of the above liquors by means of atomizers working in the condensers; (3) the complete removal of the tars produced in the operation; (4) the passing of these acid tars downward over bafflers, where they are met by the upward current of gases, to which they give up the acetic acid contained in them; (5) securing by the means described a pyroligneous acid or pyrolignite of sodium of a higher degree of purity than the corresponding products obtained by the old process.

The improvements in the new process are fundamental, and any one contemplating the establishment of new works will do well to adopt them. As regards the question of acetone manufacture, direct pyroligneous acid can now be obtained by the new method at once, which acid is then available for conversion into acetone without further purification, the use of acetate of lime being no longer required. The reduction of cost by this method is stated to be about 25-30 per cent.—*U. S. Consular Report*, April 17, 1909.

Rubber Production, Brazil.—In transmitting the following statistics showing the decreased exports of rubber from Para, Manaos, Itacoatira, and Iquitos during the month of February, 1909, as compared with the exports during the same month in 1908, Consul George H. Pickerell, of Para, reports that the producers, confidently assert that the exports for March will show a still greater decrease (kilo = 2.2 pounds):

Whither exported.	Fine. Kilos.	Medium. Kilos.	Coarse. Kilos.	Caucho. Kilos.	Total. Kilos.
United States....	1,188,074	218,475	598,018	483,843	2,488,410
Europe..........	869,658	202,450	405,838	615,827	2,093,773
Total.......	2,057,732	420,925	1,003,856	1,099,570	4,582,183
Total in 1908....	2,898,641	565,910	1,027,593	1,082,724	5,574,868
Decrease.....	840,909	144,985	23,737	19,496	992,685

—*U. S. Consular Report*, April 29, 1909.

Rubber in Mexico.—Consul William W. Canada, of Vera Cruz, in reply to many inquiries from the United States, furnishes the following information relative to the condition of the rubber industry in Mexico:

I submit the following short report on the question of rubber culture in Mexico, prepared by one best qualified to give the facts, and by his permission:

The tapping was begun in October and completed the first week in February. The rubber is now well dried, except the last few sheets, and it weighs 590 pounds. This is practically the same as last year's product, but that was secured by two tappings, while this is from one only. This year we secured about 75 pounds of our crop from young trees never before tapped; the balance represents about 1 2/3 ounces per tree throughout our 10-year-old fields. The output is not particularly encouraging, as it is 8 per cent. less than last year's average, while we made this season 50 per cent. more cuts to the tree in our single tapping than we did in both tappings last year. The thrifty trees gave 50 per cent. more latex than last year, but this was offset by our losses among the backward trees, and the latex proved to be thinner than last year, as equal units of liquid measure dried down to less rubber. This was due partly to tapping higher on the trees, where the latex is necessarily poorer, and possibly steady tapping once or twice a year, for several years, may have affected temporarily the latex reserves in the trees. In view of our tapping record to date, I do not know whether to expect an increased, diminished, or stationary yield the coming season. We went into this business with our eyes open and knew that neither we nor any one else had much of any practical knowledge of the proposition. Our education has been and still is progressing as rapidly and with as little expense as anybody engaged in the Mexican rubber planting field. I have just received a letter from Tabasco, the only important rubber district in Mexico that I am not personally acquainted with. This letter is from a personal friend who recently took a position on a Tabasco rubber property, and he writes me detailed data as to size of trees of various ages, tapping yield, etc. I therefore repeat now the opinion that our trees grow as rapidly as any elsewhere in Soconusco, and our tapping results compare favorably with those in Soconusco or any other part of Mexico.

It is expected that the United States Smelting, Refining and Mining Co. will soon be given a hearing in the United States District Court on its petition to be permitted to reopen the copper smelter at Bingham Junction.

The Murray Plant of the American Smelting and Refining Co. was closed for the first half of May on account of a strike started by the Greek and Austrian laborers.

Plans have been perfected for the addition of a regrinding and concentrating plant at the United States Smelting, Refining and Mining Co.'s mill. It is hoped that by this means more iron and zinc may be saved. The Huff electrostatic zinc separator is to be used.

OFFICIAL REGULATIONS AND RULINGS.

The following judgment notices have been issued by the Board of Food and Drug Inspection.

MAY 17, 1909.

58. Adulteration and misbranding of oats (as to presence of barley).

59. Adulteration and misbranding of lithia water (basic lithia water).

60. Adulteration and misbranding of buckwheat flour (as to presence of wheat and maize).

61. Misbranding of vinegar (as to location and name of manufacturer).

62. Misbranding of vinegar (as to location and name of manufacturer).

63. Misbranding of canned corn (underweight).

May 20, 1909.

64. Misbranding of canned apples (underweight).

65. Misbranding of beer (as to quantity of alcohol).

May 29, 1909.

66. Misbranding and adulteration of stock feed (as to presence of ground corn-cobs, etc.).

67. Misbranding of butter (as to location and name of manufacturer).

June 2, 1909.

68. Misbranding of whiskey (as to presence of whiskey).

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given of the judgment of the court in the case of the United States *v.* 50 barrels of whiskey, a proceeding of libel for seizure and condemnation of said goods under Section 10 of the aforesaid act, lately pending, and finally determined by entry of a decree of forfeiture and condemnation on December 19, 1908, in the district court of the United States for the district of Maryland, wherein the Louisiana Distillery Company, Ltd., a corporation of New Orleans, La., was claimant. The so-called whiskey was misbranded within the meaning of Section 8 of the act, in that the barrels containing it were labeled and branded "Bourbon Whiskey," whereas, in fact, it was not Bourbon whiskey, but a distilled product of fermented molasses, manufactured and produced in New Orleans, La.

INTERVENTION, CLAIM, EXCEPTION AND ANSWER OF THE LOUISIANA DISTILLERY COMPANY.

To the libel of the United States for seizure and condemnation of the so-called whiskey, the Louisiana Distillery Company, the manufacturers and shippers of said whiskey, intervened and filed its claim, exceptions, and answer, wherein, as matter of exception, it was alleged that the court was without jurisdiction of the proceeding, because it did not appear from the libel "that notice was given to any person whatsoever of any analysis or examination of the whiskey attached under said libel before the libel herein was filed, as required by the act of Congress approved June 30, 1906."

The foregoing exception of the claimant having duly come on for hearing, and having been fully argued, the court overruled the exception and pronounced its ruling thereon as follows:

RULING OF THE COURT ON EXCEPTION TO JURISDICTION.

Morris, *District Judge* (orally): In this case, which is a libel for the seizure and forfeiture of 50 barrels of distilled spirits alleged to be misbranded contrary to the provisions of the act of Congress of June 30, 1906, the libel does not allege that there had been any preliminary examination such as is provided for by Section 4 of the act.

The claimant has excepted to the libel upon the ground that the court has no jurisdiction unless such a preliminary examination has preceded the seizure.

It is urged that the harshness of the proceeding in seizing goods alleged to be misbranded without giving the owner the opportunity of being heard as to their true nature is such that the court should if possible construe the law so as to require the examination as a prerequisite to seizure. Such seizures are not unusual, and it is plain that if the harshness were conceded, it would not justify the court in reading into the law a limitation which it does not contain. The act provides two different proceedings to enforce the provisions. One is by a criminal proceeding in personam; the other is by a proceeding in rem, by seizure of the offending thing itself, and forfeiture if found to be in violation of the law. In this latter case there is no provision for a preliminary examination. Section 10 of the act provides that any article of food, drugs, or liquor that is adulterated or misbranded, which is being transported from one State to another, shall be liable to be proceeded against and seized for confiscation by process of libel for condemnation. It is further provided that the proceedings of such libel cases shall conform as near as may be to the proceedings in admiralty, except that either party may demand trial by jury of any issue of fact joined in any such case. The libel alleges that fifty barrels of distilled liquor are now at a named place within the district, having been transported from the city of New Orleans, in Louisiana, to Baltimore, Maryland, branded "Bourbon Whiskey," which brand indicates a liquor containing all the congeneric substances obtained by distillation from a fermented mixture of grain, of which Indian corn forms the chief part, and confined to whiskey distilled in the State of Kentucky, and that the fifty barrels of distilled liquor in question, branded Bourbon Whiskey, are not whiskey at all but a distillate of molasses. The libel then prays that the fifty barrels of liquor may be proceeded against and seized for condemnation, in accordance with the act of Congress approved June 30, 1906, and prays the court to order process of attachment in due process of law, and that all persons having or pretending to have any right, title, or claim in said liquor may be cited to appear and answer the premises. This is according to the course of proceeding in libels in admiralty and a similar proceeding in rem for forfeitures for violation of the internal revenue laws. Such seizures are made in cases in which forfeiture of the goods is the penalty, without preliminary examination or proceedings of any kind, in cases of violation of the customs laws and the shipping regulations, as well as violations of the internal revenue laws.

The exception is overruled.

The case having duly come on for further hearing on the facts as alleged in the libel of the United States and the answer of claimant, and a jury having been demanded by the claimant, the issues were submitted to a jury upon testimony, argument of counsel, and the following instructions of the court:

INSTRUCTIONS OF THE COURT TO THE JURY.

The Court: I will not call upon counsel for the United States to reply. The case as it is presented to the jury is a very clear one. I reject the only prayer offered by the defense. Really, that prayer concedes the misbranding of the liquor, and asks me to say to the jury that if they shall find that this was done under the control and by the agents of the United States, the United States, which is the plaintiff in this case, is estopped from proceeding to condemn these goods and forfeit the goods for misbranding. That proposition I reject. Every one who deals with agents of the United States deals with them with the knowledge imputed to him of the restriction upon their authority. It seems to

me it can not be successfully contended that any agent of the United States has authority to do a thing which is forbidden by law; and it is forbidden by this law passed in 1906, the Pure Food Law, to misbrand any goods which are intended to be or are actually transported from one State to another. Of course the gentlemen of the jury would know, or should know, that the United States has no authority, under the Constitution of the United States, to regulate the sale of goods within the limits of a State. It is only when they are transported from one State to another, and become a part of interstate commerce of the country, that the United States has the authority to pass laws regulating them. So this liquor, without infraction of any law so far as I know, might have been offered for sale and sold in Louisiana, unless there is some law of Louisiana which prohibits the misbranding of or misrepresentation with regard to the constituents of an article that is offered for sale. It is only, therefore, when these goods become a part of the interstate commerce of the country that this Pure Food Law of 1906 applies to them, that "misbranding" shall apply to the placing on the package of any statement which shall be false or misleading in any particular, and provides that any article misbranded, which is transported from one State to another for sale, is liable to confiscation. Therefore I do not think that anything that was done in the distillery in Louisiana, in New Orleans, in any way estops the United States or estops the authorities, or the agents of the United States in Maryland, from proceeding to condemn these goods upon the ground that they were misbranded. It would be destructive of the enforcement of many of the laws of the United States if the act of any agent of the United States could be set up as a defense against the explicit law, the explicit law in this case being that any goods that are misbranded shall be forfeited. If any gauger, at the request of a distiller or under a generally understood practice of the distillery, should misbrand an article of liquor, it would be utterly subversive of the law if that could be said to be a defense to the positive enactment of the act of 1906 that misbranding goods that are to be transported from one State to another shall be prohibited. I, therefore, reject that contention on behalf of the claimant of the goods in this case.

Then the jury come to consider what is the real issue which they are to determine, and that is whether these goods are whiskey as known to the trade and to the community generally, and to those who deal in whiskey. If it is not whiskey, of course the case is made out in favor of the United States. If the jury believes—and there is a great deal of testimony to that effect—that the word "whiskey" is applied only to a distillate made of grain, that is an end of the case, an end of the defense in the case, their verdict must be for the United States, because it is admitted in this case, and it is not a question of dispute, that this liquor is not made from grain, but is a distillate of molasses with a slight infusion of sulphuric acid

But the jury might possibly find that it could be called whiskey. Then there is a second question, can it be called Bourbon whiskey? There is a great deal of testimony to show that "Bourbon whiskey," in its most general sense, is a whiskey made from grain of which corn is the larger constituent. If you find that this was not such a whiskey, then it is not Bourbon whiskey, and your verdict must be for the United States. Then there is testimony also to the effect that "Bourbon whiskey" as understood in the trade is confined to a whiskey made in Kentucky. If you find that to be the fact—and that is for you to decide entirely on the testimony—if you find that in the trade and among those who deal and who are familar with the article "Bourbon whiskey" implies that it is made in Kentucky, then of course that is an end of the case so far as the claimant is concerned, because it is admitted that this liquor was made in New Orleans.

I might say that a good deal has been said about the hardship and injustice of condemning an article which once has been branded by the gauger, but I do not think that that appeals very strongly to any one's sense of morality, because a gauger is not a man who is to decide what is the trade name of an article. He takes that largely from the distiller. He is not a dealer in liquor, nor is he a man of science who is to determine once for all, and incontestably, whether it is what it is branded, or something else.

I will now give you the instructions asked for by counsel for the United States. The first prayer is as follows:

The jury are instructed that if from the evidence they shall find the word "whiskey" as understood by scientific men, the liquor trade, and the public generally is confined to a distillate of grain, and shall further find that the contents of the barrels libeled in this case is a distillate of molasses, and that the said barrels were branded Bourbon whiskey, then the said barrels were misbranded, and their verdict must be for the libelant.

The second prayer has reference to the restricted meaning of "Bourbon whiskey," as applying to whiskey distilled in the State of Kentucky. It is as follows:

The jury are instructed that if they shall find from the evidence in this case that the phrase Bourbon whiskey as defined in the standard works of reference in use in this country, and as understood by scientific men, the liquor trade, and by the public generally, imports a liquor distilled in the State of Kentucky, and shall further find that the contents of the barrels libeled in this case were distilled in New Orleans, in the State of Louisiana, and shall further find that the said barrels were branded Bourbon whiskey, then the barrels were misbranded, and their verdict must be for the libelant.

The third prayer has reference to what you may find from the evidence is the more general acceptation of the words "Bourbon whiskey," and that does not necessarily require that it shall be made in Kentucky. The instruction is as follows:

The jury are instructed that if they shall find from the evidence that the phrase Bourbon whiskey as understood by scientific men, the liquor trade, and the public generally, is confined to a distillate of grain made from the mixture of fermented grain, of which mixture corn constituted the greater part, and shall find that the contents of the barrels libeled in this case are a distillate of molasses, and shall further find that the said barrels are branded Bourbon whiskey, then the said barrels are misbranded, and their verdict must be for the libelant.

I do not think that there is anything that I need say to the jury further, except to remind you that there is no dispute at all as to the material out of which this distillate was made. The whole case, in my judgment, and I so instruct you, turns upon whether the general acceptation

of the word "whiskey" imports that it is made from grain. Of course this liquor was not so made.

Further, in regard to Bourbon whiskey, if the term "Bourbon whiskey" implies that the article was made of corn in greater part—not made of molasses but made of grain of which corn was the greater part—then of course it was misbranded.

So, further, if you find that "Bourbon whiskey" is confined to whiskey made in Kentucky, and of grain, and that the larger constituent part must be corn, then of course this would not be "Bourbon whiskey," because it was not so made.

As to what the testimony has convinced you are the proper meanings, accepted by the trade and by scientific men, of "whiskey" and "Bourbon whiskey," these are facts to be found by you from the testimony, which I leave entirely to you. It is my duty to instruct you upon the law and to leave the facts to be found by you.

The jury having returned a verdict that the said whiskey was misbranded, on December 19, 1908, the court rendered its decree thereon in substance and in form as follows:

IN THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF MARYLAND.

UNITED STATES OF AMERICA
vs.
FIFTY BARRELS OF WHISKEY.

The claimant in this cause, having demanded trial by jury of the issues of fact joined hereinbefore, and the said trial by jury having been duly had, and the jury by its verdict having found that the articles libeled in this case were misbranded, in that they were branded "Bourbon Whiskey," and the pleadings and the said verdict of the said jury having been considered and due deliberation having been had.

It is ordered, adjudged, and decreed, this 19th day of December, 1908, that the articles in this case be, and they are hereby, condemned, and the marshal shall completely destroy the same on the eighth day of January, in the year 1909, or so soon thereafter as the said marshal can conveniently complete such destruction, provided, however, that the said article shall be delivered to the claimant thereof, if on or before the fourth day of January, 1909, the claimant shall have paid all the costs of these libel proceedings, and shall have executed to the United States of America a good and sufficient bond in the penal sum of four thousand dollars, with a surety or sureties to be approved by this court, or to the clerk thereof, conditioned that the said articles so libeled shall not be sold or disposed of contrary to the provisions of the Food and Drugs Act of June 30, 1906, or to the laws of any State, territory, district, or insular possession.

THOMAS J. MORRIS, *District Judge.*

The facts in the case were as follows:

Investigation by an inspector of the United States Department of Agriculture of the distillery of the Louisiana Distillery Company at New Orleans, La., disclosed that for several years prior thereto the distillery had produced no spirit made from grain mash, but only a product from molasses and water. Subsequent to this investigation, and during the month of November, 1907, evidence was procured that the Louisiana Distillery Company had shipped 50 barrels of whiskey from New Orleans to A. L. Webb & Sons, Baltimore, Md., by whom they were received on the 16th day of that month. Each barrel was branded "Bourbon Whiskey." In addition to the evidence procured by the aforesaid inspector, the dump sheets in the possession of the collector of internal revenue for the New Orleans district disclosed that the so-called whiskey was a product of fermented molasses. It was apparent, therefore, that the article was not Bourbon whiskey, and that the branding of it as such was false, misleading, and deceptive within the meaning of Section 8 of the Food and Drugs Act. Accordingly, on November 25, 1907, the Secretary of Agriculture reported the facts to the United States attorney for the district of Maryland, who forthwith filed a libel for seizure and condemnation of the so-called whiskey, with the result hereinbefore stated.

H. W. WILEY,
F. L. DUNLAP,
GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved:
JAMES WILSON,
Secretary of Agriculture,
Washington, D. C., May 14, 1909.

(T. D. 1498). *Adulterated Butter.*—Modification of regulations relating to procuring samples of adulterated butter, and permitting payment of tax due on adulterated butter under seizure by the owner or custodian of the same.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., May 17, 1909.

To collectors, internal-revenue agents, and others:

Upon representations by a committee of those engaged in the butter trade, and after a careful investigation into the subject through officers and agents of this bureau in the field, the conclusion has been reached that under the conditions existing the inspection, sampling, seizure, and formalities incident to the enforcement of the act of May 9, 1902, defining and imposing a tax upon butter as adulterated which contains an abnormal per cent. of moisture, have in many cases worked a hardship upon those engaged in this industry, and to obviate this it has been decided to adopt the following plan for the execution of this work in the future:

First, no samples of butter which, upon preliminary tests by the officers taking the same, show less than 16 per cent. of moisture should be forwarded to the laboratory of this office, and only one sample out of every ten, or from every tenth package, found to contain abnormal moisture, if the owner of the butter agrees to accept the preliminary test as conclusive, will be so forwarded; otherwise a sample out of every package will be taken and submitted to this office. The samples taken by officers for the preliminary tests should not exceed 3 ounces in quantity, while those to be forwarded to the laboratory of this office should not exceed one-half pound, taken after the method or manner prescribed in T. D. 1449 of January 2, 1908. The preliminary tests should be made immediately by those taking the samples, and if found to be less than 16 per cent. moisture the goods should be at once released, provided detention or seizure has formally, or by agreement, been made.

Second, for the purpose of relieving those in the butter trade of the loss or burden through the delay and formalities incident to forwarding samples to this office for analysis, formal seizures of the butter found upon the preliminary tests to contain 16 per cent. or more of moisture, and its detention until payment of the tax thereon has been made, officers are instructed to release all the butter thus found to be adulterated upon the payment of the tax due thereon by the ostensible owner or person in whose custody the same shall be, upon condition that said butter shall be reworked and the excess of moisture removed therefrom before the same is sold.

Goods may be thus released without waiting for the report of the official chemist upon the sample forwarded to this office, which, if corroborative of the preliminary test, would in no wise affect the status of the case, but if in contradiction to the preliminary test analysis proved that the butter did not contain abnormal moisture a claim for the refund of the amount overpaid will be entertained upon presentation through the office of the collector to whom such overpayment was made. Collectors will be required to see that adulterated butter so released is not placed on the market for sale until the excess of moisture is removed or proper steps taken for the necessary reworking.

Officers taking samples of butter are directed to use great care to avoid mutilation and consequent loss to the owners of the goods sampled, and they are authorized to pay for the actual quantity taken and found to be not adulterated at the current wholesale price of the particular grade or brand of goods and include this expenditure in their accounts. In all cases before taking samples officers should notify the owners of the butter, or the person having custody of the same, of their intention to sample the goods, so as to allow the owners to be present, and also to take samples of the butter in question, if they so desire, but as these duplicate samples will not be necessary in the Government test the expense of same will have to be borne by the owner.

All rules or decisions heretofore published in conflict with the above are hereby modified and revoked in so far as is necessary. A strict compliance with this decision by the officers in the field charged with the enforcement of the law will obviate much of the delay and burden complained of by those engaged in the butter business.

ROBT. WILLIAMS, JR.,
Acting Commissioner.

Approved:
FRANKLIN MACVEAGH, *Secretary of the Treasury.*

(T. D. 29781). *Drawback on Aluminum Alloy.*—Drawback on aluminum alloy manufactured by the Northern Aluminum Company, of New Kensington, Pa., with the use of imported aluminum.

TREASURY DEPARTMENT, May 25, 1909.

SIR: On the exportation of aluminum alloy manufactured by the Northern Aluminum Company, of New Kensington, Pa., with the use in part of imported aluminum, a drawback will be allowed equal in amount to the duty paid on the imported material used, less the legal deduction of 1 per cent. * * * * *.

The drawback entry must show the total quantity and weight of each kind of alloy exported and the quantity of imported aluminum used in the manufacture thereof. Said entry must further show, in addition to the usual averments, that the exported product was manufactured of the materials and in the manner set forth in the manufacturer's sworn statement, dated February 27, 1909, transmitted herewith for filing in your office.

In liquidation, the quantity of imported aluminum which may be taken as the basis for the allowance of drawback may equal that declared in the drawback entry, after official verification of exported quantities and determination by chemical analysis of the percentage of aluminum contained in the exported product, provided such allowance shall not exceed the quantity determined by analysis with an addition thereto of 1 per cent. to cover wastage.

Samples shall be taken of each shipment or sworn samples furnished as required by the collector.

Respectfully, JAMES B. REYNOLDS,
(63567). *Assistant Secretary.*

COLLECTOR OF CUSTOMS, *Philadelphia, Pa.*

(T. D. 1502). *Oleomargarine.*—Modification of T. D. 1472, concerning packing of coloring matter in manufacturers' original packages of uncolored oleomargarine.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., May 26, 1909.

To Collectors, Revenue Agents, and Others:

As a result of recent discussion of the provisions of T. D. 1472, it is deemed proper to modify in some particulars the language of that letter of instructions to officers and others, so that any legal complications likely to arise in carrying out the same may be avoided.

To accomplish this end T. D. 1472 will be construed as holding that while the law does not specifically and in exact terms prohibit the packing of small quantities of coloring matter in manufacturers' original packages, it is a practice this office can not approve, because of the opportunity it affords for the perpetration of frauds on the revenue.

Any manufacturer of oleomargarine who packs coloring matter in his original packages will do so at his own risk, and if the product so packed is found on the market in the hands of any person intending to manufacture the same into articles subject to tax for the purpose of fraudulently selling such manufactured article, or with design to evade the payment of said tax, the same will be seized and shall be forfeited, as provided by Section 3453, Revised Statutes.

T. D. 1472, so far as the same is in conflict with the foregoing, is hereby rescinded.

In this connection attention is invited to T. D. 1333.

ROBT. WILLIAMS, JR., *Acting Commissioner.*

(T. D. 29800—G. A. 6912). *Anthracite Coal.*—Welsh anthracite coal containing between 90 and 92 per cent. of fixed carbon is free of duty under Section 2, act of January 15, 1903 (32 Stat. 773; T. D. 24164), providing that after said date paragraph 415, tariff act of 1897, should not "be construed to authorize the imposition of any duty upon anthracite coal."

(T. D. 29805). *Wool Olein.*—Swan & Finch Company *v.* United States.

U. S. Circuit Court, Southern District of New York. May 13, 1909. Suit 5426.

WOOL OLEIN—WOOL GREASE—DISTILLED OIL.

Wool olein, an oil distilled from wool grease, is not "wool grease" within the meaning of paragraph 279, tariff act of 1897, but is dutiable as a distilled oil under paragraph 3.

On application for review of a decision by the Board of United States General Appraisers.

(Decision in favor of the Government.)

The decision below, which is reported as Abstract 20159 (T. D. 29442), affirmed the assessment of duty by the collector of customs at the port of New York. The Board's opinion reads as follows:

CHAMBERLAIN, *General Appraiser:* The merchandise in question, described on the invoices as olein, consists of a dark reddish oil distilled from wool grease. It was returned as an acid not specially provided for, and duty was assessed thereon at the rate of 25 per cent. ad valorem under paragraph 1 of the tariff act of 1897. The importers claim the merchandise to be dutiable under paragraph 279 of said act at one-half cent per pound as wool grease.

At the hearing the examiner who passed the merchandise testified that his return was erroneous and that the merchandise should have been returned as a distilled oil under paragraph 3, dutiable at 25 per cent. ad valorem. That the same is a distilled oil is very conclusive, for an examination of the evidence shows that not only the Government witness but the importers' witness testified that the article is a *distilled oil*. The sole question, then, is whether the article is or is not commercially known as wool grease. This the importers failed to prove, for the reason that one interested witness is insufficient to establish commercial designation. Neuss *v.* United States (142 Fed. Rep., 281; T. D. 26597); Berbecker *v.* Robertson (152 U. S., 373).

Furthermore, in G. A. 6084 (T. D. 26539) the Board had before it for consideration similar merchandise, and the claim of the importers that the merchandise should be admitted as wool grease was not upheld, it being held dutiable as a distilled oil. A comparison of the chemical analysis of the article here in issue and that passed upon by the Board shows but slight variations, the specific gravity, the free fatty acids, and the unsaponifiable matter being almost identical.

It is our opinion that the article under consideration is a distilled oil, that it is not wool grease, and that it is not known in trade as such. We hold it is properly dutiable under paragraph 3 as a distilled oil, and overrule the protests without affirming the action of the collector.

Brooks & Brooks (*Frederick W. Brooks* of counsel), for the importers.

D. Frank Lloyd, assistant United States attorney, for the United States.

PLATT, *District Judge:* The article in controversy was invoiced as olein, but is shown by the testimony to be also known as wool olein or "wooleine." It is described by the Board of General Appraisers as consisting of "a dark reddish oil distilled from wool grease." By an admitted error it was classified as an acid. The Board, without approving the collector's assessment, held that it should have been classified as a distilled oil under paragraph 3, tariff act of 1897, and overruled the importers' contention for classification under paragraph 279 as "wool grease."

I am of the opinion that the Board should be affirmed. For one thing, there being evidence to support their finding that the material in dispute is not wool grease, I am bound by that finding. But aside from that consideration, I think that if I had been the Board I should have decided as they have.

In Movius *v.* United States (66 Fed. Rep., 734) wool grease was said to be of a "viscous consistency," while the substance at bar is an oil and, being distilled from wool grease, should be considered as a product of that material, rather than wool grease itself. It is not the "crude raw material" referred to by the circuit court of appeals in the Zinkeisen case (167 Fed. Rep., 312; T. D. 29546) as being the article intended by Congress to be covered by the expression "wool grease."

Decision affirmed.

NOTE.—No appeal will be taken in this case.

REGULATIONS.

(1) Viruses, serums, toxins, and analogous products propagated in licensed establishments and imported from abroad shall be detained by customs officers at ports of entry, pending examination by officers of the Public Health and Marine-Hospital Service as to purity and potency, and as to whether said products are properly labeled, as required by Section 1 of the act above referred to.

(2) Samples of the same laboratory numbers shall accompany each foreign importation of viruses, serums, toxins, and analogous products, and said samples shall be forwarded by collectors of customs to the Surgeon-General of the Public Health and Marine-Hospital Service at Washington for examination.

(3) Viruses, serums, toxins, and analogous products imported from foreign countries shall be refused entry by collectors of customs unless propagated in an establishment holding an unsuspended and unrevoked license, or intended for examination precedent to obtaining a license. Collectors and other officers will be advised from time to time as to the establishment duly licensed in accordance with said act.

(4) The term viruses, serums, toxins, and analogous products shall include the following and such other preparations as may be designated by the Secretary of the Treasury from time to time:

Antidiphtheric serum, or diphtheria antitoxin.
Antitetanic serum, or tetanus antitoxin.
Antistreptococcic serum.
Antistaphylococcic serum.
Antigonococcic serum.
Antipneumococcic serum, or antipneumonic serum.
Antidysenteric serum.
Antituberculous serum.
Antipest serum, or antiplague serum.
Streptolytic and pneumolytic serum.
Antimeningococcic serum.
Erysipelas and prodigiosus toxins.
Tuberculins.
Emulsion of tubercle bacilli.
Suspension of lactic acid bacilli.
Antityphoid serum.
Bacterial vaccines.
Normal horse serum.
Vaccine virus.

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EDITORIALS.

THE DETROIT MEETING.

President Whitney struck the keynote of the General Meetings of the American Chemical Society when he said that the purpose of the gatherings was not so much to listen to papers as to get acquainted: knowledge of a man's personality was the basis of appreciation of what he said or wrote. Chairman Little, of the Division of Industrial Chemists and Chemical Engineers, put the idea to work when he asked each member of the Division to rise, state his name and deliver a brief autobiography. A confession is always thrilling and there was the most intense interest manifested in these brief statements of careers and occupations. Afterward every man and woman felt better acquainted. This precedent should become a custom and a tradition in the Division.

The Detroit meeting was the most successful summer meeting ever held by the Society. Two forces accomplished this result: a growing and enthusiastic membership, officered by men of worth, breadth and great activity, and the hosts, the Society of Detroit Chemists. Whether judged by the attendance, which was over three hundred, the number of papers read, which was more than one hundred and seventy, or by the general enthusiasm and good fellowship this meeting sets a new mark for summer meetings of the Society.

Next winter's meeting will be held in Boston; next summer's meeting in San Francisco. If any chemist, who is not in the habit of attending these meetings, desires to be inspired with a new interest in his profession, let him attend.

The officers of the American Chemical Society are to be congratulated on their splendid organization.

THE LIMITATIONS OF THE CHEMIST.

We all know what a halo of mystery and romance clung to the alchemist of old, especially in the minds of his contemporaries. His profound skill and wisdom were regarded as almost supernatural. It is without doubt helpful to the dignity of the profession to-day that something of the same feeling of awe and wonder exists in the popular mind toward the modern chemist. To the "laity" he still works in dark and mysterious ways and is endowed with keener and more occult powers than his fellows. With practically no difficulty he is supposed to be able to solve at once any complicated industrial problem suggested, or duplicate, perhaps while you wait, almost any unknown mixture of ingredients placed in his hands. With scarcely an effort he is considered capable of detecting the presence and amount of any obscure substance whatever, poisonous or otherwise.

In fact, in the popular eye the chemist of to-day is still apparently gifted, to some extent, like the alchemist of yore with superhuman powers. Fortunate it is that, as a rule, no one knows better his limitations than the chemist himself, and this knowledge affects his life and work in widely varying degree, largely dependent, of course, on

the character of his work and his temperament. To a large number the realization of these limitations will make little or no practical difference, while with others it may act as a continual source of annoyance. There is the superconscientious worker, for instance, who worries often unnecessarily lest perchance in his determination of alcohol, some other unidentified volatile substance may not also be included, or lest, when required to report the miscellaneous ingredients of a mixture, something important and even vital may not still be undetermined.

The extent to which one's limitations seriously affects one's work largely depends on the degree of responsibility bound to arise eventually from the results of that work. Probably, from the nature of his calling, no one is more handicapped in this regard than the toxicological chemist. To him at times may come the responsibility of causing a fellow being to be condemned to death or long imprisonment by evidence submitted by himself. Under such conditions he cannot fail to consider in every phase the possible fallibility of his tests and of his opinions based thereon.

To a less degree does the same question of limitations apply to the public analyst who alleges adulteration or misbranding of food, or, indeed to all chemists who at times appear as expert witnesses and on whose evidence decisions are rendered in court. The anomaly is familiar to us all of the method that works so admirably in one man's hands proving utterly useless with another. This illustrates a single phase of the chemist's limitations. Can we not attribute to these very limitations the fact that so often diametrically opposite testimony is given in court by experts of equal ability and integrity, or that glaring differences of opinion are expressed and widely varying results obtained by scrupulous workers employing equally careful methods of analytical research? Better by far that this be the case rather than the oft-repeated popular taunt that experts will testify to anything they are paid for.

The proper recognition of these limitations, not in a pessimistic spirit, but as a prevailing condition, cannot fail to help rather than hinder the progress of the art. Such recognition need not discourage work in any field, but should rather stimulate to increased care and precaution in methods of procedure, and to greater tolerance of those who honestly differ from us.

ALBERT E. LEACH.

THE CHEMIST AND THE PUBLIC.

IT is altogether natural that the public recognition and appreciation of the chemist should be a slow development. That which is occult, obscure, unseen, dark, may excite the imagination of the layman but will surely appeal less strongly to his rational understanding. The art of the engineer has ever been visible and tangible, and therefore has been the more readily grasped and appreciated by the average man. Not so the art of the chemist.

It is gratifying to note that in these latter days many signs of an increasing understanding of the chemist's aims and works are being shown, if not by the general public, at least by the non-technical educated minority. Many things have worked toward this end—the chemist's part and the public's interest in the conservation of natural resources, the development of manufacture and industry and better and more liberal education itself. As a sign of the times the following editorial from the *Boston Herald* of June 26th, is of the greatest interest. It is entitled "The Chemist's Service."

"Two sorts of wise men are now interested in the chemist: the man who is concerned with the origins and elements of all life and the man who is bent on developing human welfare to its utmost on the physical side. The philosopher is interested in him because, just now, more than any other man of science, the chemist seems to be in line as the agent for revealing unsuspected and revolutionizing facts about nature and her laws. Where a decade or two ago the biologist was supreme the chemist now stands as pioneer in fathoming, not the source, but the method of continuous creation. The stateman, the manufacturer, the merchant and the consumer of the products of applied science are interested in the chemist, because wherever he has been given a fair chance by private initiative or by generous treatment on the part of the state, he has added so immensely to the wealth of society and to the comfort and the health of life by his discoveries, by his reductions in cost of manufacture, by his utilization of matter previously wasted, by his synthetic creation of rare and costly products of nature and by the light he has shed on the hidden causes of health and disease through study of the chemistry of transformations that go on within the body, that it is difficult to overrate his importance to society.

"The debt owed the chemist is one that cannot be measured in pecuniary terms; it must be reckoned in higher values that always follow after bettered

economic status, better health, lessened labor and increased efficiency, not to mention relative freedom from pain and absence of worry. The chemist has added millions of dollars to the capital of nations sensible enough to foster his education and to equip him with laboratories and to set him at work in agriculture, manufacturing and commerce. He also has been a life-saver, a life-prolonger, an agent in transforming the outlook of wise farmers, and in rescuing adults and children from the toils of adulterators of foods. Consequently he deserves generous and respectful treatment by his countrymen.

"The practical side of this matter is simple. If the United States, if New England, if Massachusetts, are to be as wise as they need to be in order to compete with rivals like Germany or Japan, or with American states that have amply equipped universities strong in their scientific equipment, then they must give increased attention to the matter of training men for applied chemistry, men who can do for New England's barren soil and manifold industries what chemists in Germany, Switzerland and Japan have done for those not overfertile lands.

"If conditions at Harvard call for not less than $1,000,000 necessary to put its chemical laboratory, with its staff of expert investigators, in a position to do first-grade work under normal conditions, then there are imperative reasons why Harvard's well-to-do friends should respond to an appeal for aid. Nor is the case different with the "Tech," with the State Agricultural College or any institution in New England which includes in its working plan of service the training of chemists for practical aid in agricultural or manufacturing production, or in the conservation of resources, by the protection of health and the protection from disease."

ORIGINAL PAPERS.

OIL SHALES OF AMERICA.[1]

By Charles Baskerville and W. A. Hamor.

Received May 10, 1909

The use of shale as a source of oil by destructive distillation is well known in England, Scotland, France, Germany, New Zealand, and Australia. In America, however, this fact is not so well recognized, although Gesner claimed to have been the first to produce illuminating oil from bituminous materials on this continent. At public lectures delivered in Prince Edward's Island in August, 1846, he burned in lamps the oil obtained by distilling coal.[1] Patents granted to Gesner nine years later[2] passed into the hands of the North American Kerosene Gaslight Company, who manufactured the oil at their works at Newtown Creek, Long Island, and sold it under the name of "kerosene oil."[3] The agents of this Company encountered considerable difficulty in selling their product.

In 1853, the United States Chemical Manufacturing Company began working coal tar for the manufacture of lubricating oil at Waltham, Mass., and in 1857, the Downer Kerosene Oil Company[4] first made mineral oils from Albert coal mined in New Brunswick, Canada. The works of Downer in Boston were erected at a cost of half a million dollars, and at Portland, Maine, he also erected a smaller works for distilling imported coal. About this time, the New Bedford Company, of New Bedford, Mass., commenced the distillation of Boghead coal, imported from Scotland, but later substituted domestic Breckenridge coal and West Virginia coal for the imported material. In 1859, six plants were erected by various companies near Pittsburg, Pa., and one of these (the Lucesco Company) had a distilling capacity of 6000 gallons of crude oil per day. Many of the companies in operation worked under licenses from the Young Company of Scotland.

In 1860, there were nearly sixty coal oil companies in existence in the United States, many of which were of small capacity. Most of them were not more than fairly started when the discovery of petroleum paralyzed the industry, and the owners were threatened with considerable loss, from which some were rescued by converting their oil works into petroleum refineries, which was accomplished with little outlay of time or money.

The following minerals were used for the production of crude oil in the United States:

[1] Taken from a paper read before the New York Section of the Society of Chemical Industry, April 23, 1909.

[1] "A Practical Treatise on Coal, Petroleum, and Other Distilled Oils," 2nd Ed., 1865, p. 9.

[2] U. S. Patent 12612, March 27, 1855.

[3] The North American Kerosene Gaslight Company, which was organized in 1854, first worked under the patents of J. H. and G. W. Austin.

[4] This Company was founded by Samuel Downer, of Boston. The latter first put an oil on the market, using the process of Luther Atwood, which consisted in distilling coal tar (1850). The product was sold under the name "coup oil" and was used for lubrication (Chandler, *J. Soc. Chem. Ind.*, **19**, 612).

Mineral.[1]	Yield of crude oil in gallons.
Albert coal (albertite[2])	110
Asphalt rock, New Brunswick	64
Pictou shale, Nova Scotia	47
Breckenridge Cannel coal[3]	130
Erie Railroad coal	47
Newburg coal	72
Falling Rock coal	80
Pittsburgh coal	49
Kanawha coal	71
Elk River coal	60
Cannelton coal	86
Coshocton coal	74
Ouachita brown coal	68[4]
Ouachita bitumen	64
Ritchie County bitumen (Grahamite)	170

Oil shales occur on the Humboldt River, opposite to Elko, Nevada; on the Big Blackfoot River and near Great Falls, Montana; and in the Cholame Valley, north of Parkfield, California. Some of these are of good quality but none has been worked to any extent.

During the year 1859, the North American Kerosene Gaslight Company imported upwards of 20,000 tons of Boghead coal for the supply of their works at Newtown Creek, Long Island, at an average cost of $18.00 per ton. It was found that a ton of this mineral run in common retorts yielded 120 gallons of crude oil per ton, which gave 65 gallons of lamp oil, 7 gallons of paraffin oil, and 12 pounds of paraffin wax. The cost of the oil was estimated at 63 cents per gallon.[5]

The bituminous shales of New Brunswick, or the "Albert shale," first came into prominence through the discovery at the Albert mines of the peculiar mineral albertite.[6] The discovery of albertite was followed by a contention as to its nature, as this involved its ownership.[7] The testimony offered in the trial was of the most discordant character, and it was adjudged that

[1] See Gesner, "A Practical Treatise on Coal, Petroleum, and Other Distilled Oils," 1st Ed., **1861**, 34; and T. Antisell, "The Manufacture of Photogenic, or Hydrocarbon Oils from Coal and Other Bituminous Substances, Capable of Supplying Burning Oils," **1859.**

[2] This material was retorted at the Downer Kerosene Oil Works in South Boston; at the Downer Kerosene Oil Works in Portland, Me.; and at the New Brunswick Oil Company's Works in St. John, N. B. These companies were under contract with the Albert Mining Company from **1860** to **1864.**

[3] This material was mined in Breckenridge County, Kentucky. The crude oil yielded 58 per cent. burning oil and 12 gallons paraffin. For the yield of crude oil of various Kentucky coals, see *Second Report, Geol Survey Kentucky*, **1856–7**, 211. Breckenridge coal sold at Cloverport, Ky., for $5.00–6.00 per ton.

[4] The crude oil from this brown coal was semi-solid at 80° Fahr. It is said to have yielded 143 pounds of paraffin per ton. The material was mined along the Ouachita River, Ark.

[5] Report of the Committee, North American Kerosene Gaslight Company, New York, **1860.**

[6] See C. T. Jackson, *Proc. Boston Soc. Nat. Hist.*, **3**, 279.

[7] Suit of A. Gesner *vs.* the Halifax Gaslight Co.

the material was of the nature of coal.[1] This supposition was soon abandoned, however, and the material was regarded as a highly altered pitch or bitumen.[2] Two analyses of albertite are given here:

	Wetherill.[3] Per cent.	Gesner.[4] Per cent.
Carbon	86.307	85.400
Hydrogen	8.962	9.200
Nitrogen	2.930	3.060
Sulphur	traces	a trace
Oxygen	1.971	2.220
Ash	0.100	0.120
Total	100.000	100.000

Albertite yielded 110 gallons of crude oil per ton, of which 70 per cent. was made into lamp oil and 10 per cent. into heavy oil and paraffin. As might be expected from its low sulphur content, the oils produced from albertite were almost without offensive odor, and the burning oil was admirably adapted for burning in paraffin lamps. Albertite was also used for gas enriching, and, to a limited extent, in the preparation of cements.[5] Between the years 1863 and 1874, 154,800 tons of this mineral were mined, and it is estimated that in all over 200,000 tons were yielded by the veins in Albert County. The high price obtained, from $15.00 to $20.00 per ton, rendered albertite one of the great mineral assets of New Brunswick. The large vein has not been entirely worked out, and several smaller veins have been proved.

The "black band" shales of New Brunswick were distilled at the Caledonia Works, in Albert County, and yielded 63 gallons of crude oil per ton, while poorer beds on the Memramcook River, in Westmoreland County, were found to give only 37 gallons. Numerous leases were taken out in 1865 for operations on the bituminous shales of New Brunswick, and a company in Westmoreland County erected 100 retorts, with the design of subjecting 100 tons per day to distillation.[6] These shales pro-

[1] See C. T. Jackson, "Report on the Albert Coal Mine," Boston, 1851; and R. C. Taylor, "Deposition Respecting the Asphaltum Mine at Hillsborough, N. B.," Philadelphia, 1851. Also Bailey, *Trans. Roy. Soc. Canada*, **7**, 77; Church, *Chem. News*, **6**, 122.

[2] Taylor, *Proc. Am. Phil. Soc.*, **5**, 241; Hitchcock, *Am. J. Sci.* [2], **39**, 267; Peckham, *idem.* [2], **48**, 362; Geinitz, *Sitz. nat. Ges. Isis*, **1871**, 87; Honeyman, *Min. Mag.*, **7**, 77; Blake, *Trans. Am. Inst. Min. Eng.*, **18**, 563; Rutherford, *J. Fed. Can. Min. Inst.*, **3**, 40; and Ells, "The Geology and Mineral Resources of New Brunswick," **1907**, 107.

[3] *Trans. Am. Phil. Soc.*, **1852**, 353.

[4] *Loc. cit.*, p. 23.

[5] Some specimens of wood and brick cemented by a material composed partly of albertite have been in the Museum of the University of New Brunswick for 60 years, and show no visible change in texture or cementing power.

[6] J. W. Dawson, "Acadian Geology," Edinburgh, 1865, 2nd Edition. Ells (*Summary Report, Geol. Surv. Canada*, **1902**, A363) states that works for the extraction of oil from the black shales at

duced 7500 cubic feet of gas per ton (about one-half of the quantity yielded by albertite), and 1230 tons, valued at $3075.00, were exported in 1865.

The Utica shale was distilled in the township of Collingwood, Ontario, in 1859, as a source of oil, and it was learned that similar shales occur in the Devonian formation in Bosanquet, Lambton County, Ontario. In 1871, D. C. Glen exhibited samples of these shales in England.[1]

Over 2000 tons of oil-coal were raised near Pictou, Nova Scotia, in 1859, mostly from Frazer's mine. The following were found to be the yields from the oil-coals worked in Nova Scotia at this time:

Locality.	Gallons of crude oil per ton.
McLennan's Brook	40
Coal Brook	53
McCullock's Brook	77

This oil-coal has been described by H. How.[2]

Oil shale has been found more recently at Macadam's Lake, on the north side of East Bay, Cape Breton, Nova Scotia. This shale yields 15–20 gallons of crude oil per ton.

Near Deer Lake, in the east of Newfoundland, occurs a dark gray shale which is highly bituminous in parts.[3] This deposit has never been worked to any extent.

The large body of peculiar black, brown, and gray shales, which occur in Albert and Westmoreland counties, New Brunswick, have long been known under the name of "Albert shale."[4] The mode of occurrence of these heavy oil shales is quite distinct from that of albertite. In the case of the latter, the mineral occurs in the form of true veins, which sometimes follow the lines of stratification of the enclosing shales, but which also frequently traverse them at well defined angles. The oil shales, however, occur as true interstratified beds in the bituminous shale series. As to the geological position of the shales as a whole, it may be remarked that somewhat diverse opinions have been held from time to time by different geologists. In the early days of the investigation of these shales, it was supposed they represented an integral part of the lower carboniferous portion. This conclusion was reached from the presence in certain of the bands of shale of the remains of fossil fishes and plants, which were then supposed to have a lower carboniferous aspect and to definitely fix their horizon. From investigations made in 1876, however, it was found that the shales should stratigraphically be assigned to a lower horizon or be regarded as of Devonian Age, owing to their non-conformability to the true Lower Carboniferous sediments.

The principal areas most readily accessible at the present time, are at Taylorville, Albert Mines, and Baltimore. In all these localities the outcrops have been examined. A detailed description of these would be out of place in this paper, but suffice it to say that in the Taylorville district, although the area of shales exposed is limited, according to the report of the Canadian Department of Mines, four beds of high quality of shale with a total thickness of eleven feet have been uncovered. In the Albert Mines district six bands for a quarter of a mile along the stream, with a total thickness of about twenty-six feet, have been exposed. The shaft of the Albert Mines was sunk to a depth of 1500 feet. It cut numerous beds of oil shale and, in fact, work was discontinued in such deposits. What is known as the Baltimore shales are found for several miles along the north flank of the Caledonia Mountains, going west from Albert Mines, in five bands, with a total thickness of over twenty-two feet. These beds have been explored by two diamond drills and one churn drill through a depth of 900 feet. They were encountered at intervals throughout the borings.

Outcrops of several other beds of this shale have been observed near Rosevale post-office, and it is considered likely that at least two other beds may be found in this area. In fact, a band with a thickness not far from fifteen feet, not opened up, has been measured along the bank of the brook, which cuts it. A "gray shale," with an exposed thickness of about four feet, is found three-quarters of a mile to the west of the above; and four miles beyond; three other bands of brownish shales, the thickness of one being five feet, and all yielding oil, are found. Portions of the original bed of albertite remain in certain parts of the old workings, and recent investigations have disclosed the presence

Baltimore and Taylorville were erected in 1864, and that the industry was carried on for several years. Crude shale from Taylorville was also exported to ports in U. S. and sold for $6.00 per ton.

[1] *Geol. Mag.*, **8**, 88.

[2] *Am. J. Sci.* [2], **30**, 74.

[3] J. P. Howley, "Report to the Newfoundland Government on the Humber Valley," 1893, 16.

[4] R. W. Ells, *Ann. Report Geol. Surv. Canada, n. s.*, **1**, 1885, Report E, 63; *Summary Report Geol. Surv. Canada*, 1902, A 363–69; *Trans. Roy. Soc. Canada*, **12**, 276; "The Geology and Mineral Resources of New Brunswick," 1907, 107; *Trans. Nova Scotian Institute of Sci.*, **11**, part 4, 612; *J. Can. Min. Inst.*, **11**, 12 pp. (adv. reprint); and a forthcoming report which is to appear this summer among the publications of the Department of Mines of Canada.

of other veins of albertite. The immense dumps of shale, aggregating over 100,000 tons, contain large quantities of the mineral. It will be thus observed that the quantity of shale which yields oil on distillation is enormous, if not beyond measure.

A preliminary examination was conducted with a view of ascertaining the laboratory yield of oil and the products from the crude oil obtained from a sample of shale. This shale, which was obtained from the Baltimore locality, had the following physical characteristics: lustre, moderate; fracture, irregular and without natural line of cleavage; cross fracture, angular, partly inclining to conchoidal; and a specific gravity of 1.44. It was solid and compact. It burned with a dense smoky flame, when ignited with a match. The yield of gas saturated with tarry matters was large when a sample was heated to dull redness in a tube closed at one end.

The average composition of the shale was as follows:

	Per cent.
Moisture	0.35
Volatile matter	44.77
Fixed carbon	5.95
Ash { Phosphoric acid 0.30; Trace of chromium, no vanadium. Light brown color }	48.93
	100.00
Total sulphur	1.43
Sulphur in coke	0.20
Nitrogen	1.96

A laboratory retort for obtaining the crude oil was constructed of cylindrical cast-iron, 24 inches long and 4 inches in diameter. This retort was closed at both ends by removable caps, and at one end a 3/4 inch pipe was inserted for leading the vapors to a coil condenser, to which were attached two supplementary glass condensers. The retort was heated in a furnace to a low red heat. No difficulty was experienced in condensing the vapors evolved, as all the condensers were kept packed in ice and the distillation was allowed to proceed slowly. The distillation was made repeatedly with five pound charges. Run-of-mine material gave 55 gallons per ton (2000 pounds) of a crude oil, greenish black in color and somewhat tarry. It had a specific gravity of 0.93. The residue, or spent shale, had the appearance of burned coke. The oil "refined" in the laboratory by variations of the Tervet method[1] gave:

[1] Redwood, "Petroleum and Its Products," **2**, 644; Allen, "Commercial Organic Analysis," 1907, **2**, ii, 39.

	Per cent.	Gallons per ton
Naphtha (0.72)	9.09	6.9
Light oil (0.79)	16.57	12.0
Heavy oil (0.916)	14.00	7.8
Paraffin	7.54	35.0 lbs.
Total yield of products	47.20	
Loss	52.80	280 lbs

This preliminary examination, which was not intended to be exhaustive, indicated that the shales were worthy of more extensive investigation; therefore, some forty odd tons of the run-of-mine shale were put through the experimental plant of the Pumpherston Oil Co., Ltd., near Edinburgh, Scotland, in the presence of Dr. R. W. Ells, representing the Canadian Government, and one of us (W. A. H). This commercial test gave 48 U. S. gallons of crude oil (naphtha not recovered) and 77 pounds of ammonium sulphate per long ton.

The crude oil possessed a brownish black color, and had a specific gravity of 0.92, a flash-point of 194° Fahr. and a setting-point of 54° Fahr. It was found to contain 0.62 per cent. sulphur. It had a heating value (by bomb calorimeter method) of 18,474 B. T. U.

The crude oil is probably of a semi-asphaltic base nature. When distilled in an Engler distillation flask at the rate of 2.5 cc. per minute up to 740° Fahr., a ten per cent. residuum, soluble in carbon disulphide, was obtained. This may perhaps be increased by air-blowing. This phase of the investigation is to be pursued further.

A considerable amount of uncondensed gas was produced from the shale during retorting; in fact, this gas served to carry out the retorting. Several samples of the gas were taken at a point between the ammonia scrubber and retort combustion chamber and analyzed, with the following results:

	Per cent
Carbon dioxide	29.67
Carbon monoxide	5.06
Olefines	1.33
Methane	11.02
Hydrogen	52.92
	100.00

Calorific value, 305.1 B. T. U. per cubic foot (N. T. P.).

Sp. Gr., 0.613 (air, 1).

Weight per cubic foot, 0.0492 pound.

On refining, the crude oil gave the following yields per ton of shale[1] (23):

[1] The authors are greatly indebted to Mr. Wm. Fraser, managing director, Mr. James Bryson, works manager, and Mr. E. M. Bailey, chemist, for many courtesies during the investigation at the main works of the Pumpherston Oil Co., Ltd., at Pumpherston, Mid-Calder, Scotland.

	Brit. gal.	U. S. gal.
Naphtha	0.6	0.7
Burning oil	4.3	5.1
Gas oil	5.6	6.7
Cleaning oil	0.8	0.9
Lubricating oil	4.1	4.9
Paraffin wax	1.1	1.3
Total	16.5	19.6
Residuum	1.5	1.8
Creosote, tar, pitch, coke, etc.	22.00	26.6

The yield of refined products was regarded as satisfactory, considering the low-grade material from which the crude oil was retorted. As mentioned above, the light naphtha was lost during retorting; and, moreover, it was found impossible to extract all the lower melting-point paraffin on a small scale.

An incomplete, but sufficiently extensive chemical survey of the field was carried out to determine its value. The oil was determined by the tube test, such as is used in Scotland in testing a shale before passing it through the retorts on a commercial scale.

The tubes which were employed for the determination of the yield of crude oil from a given sample of shale, were made of 1/5 inch wrought iron tubing, having a diameter of two inches and a length of six feet, and were sealed by a cap at one end. One pound of the shale in pieces about ½ inch square was put into the tube, which was then placed in an oven and heated gradually to a dull-red heat. The tube was inserted in the oven for about a foot of its length, and inclined at a convenient angle. No condenser was used in making these tests, so that the naphtha was lost, but, by controlling the heat properly, the conditions of distillation are nearly identical with those occurring in a modern retort.

The method used for the determination of the yield of ammonium sulphate obtainable from a sample of shale was that known as the Bailey method, and which is used in the laboratories of all crude oil works where Pumpherston retorts are in use. A definite weight of the shale in small pieces (30 mm. in diameter) is heated in a malleable iron tube to bright redness in the presence of a current of steam for 1½ hours, the gases resulting being led into a flask containing 2 *N* sulphuric acid. In this solution, the ammonia is determined as nitrogen by sodium hypobromite in a nitrometer and the yield of ammonium sulphate is calculated therefrom.

Determinations by these methods approximately equal the yields obtained by retorting the shale in a Pumpherston retort.

Oil and Ammonium Sulphate taken from Different Localities

Locality	Imperial gallons of crude oil per ton	U. S. gallons of crude oil per ton	Specific gravity of oil	Pounds of ammonium sulphate per ton
Shale retorted in Scotland	40	48	0.92	77
Geo. Irving's	39	47	0.895	76
Baizley's farm, Baltimore	54	65	0.895	110
E. Stevens	49	59	0.892	67
Hayward's Brook, Prosser Brook	30	35	0.895	75
Adams Farm	43	51	0.90	93
A. Taylor's Farm, No. 1	48	58	0.91	98
A. Taylor's Farm, No. 2	37	44	0.925	110
Sample of 85 lbs. run in 1907	51	61	0.91	111

Oil shales are always of variable character, and it is impossible to procure true average samples of the various seams for examination. However, we have shown by laboratory tests that the oil shales of New Brunswick are not so variable in the yield of crude oil and ammonium sulphate as the shales of Scotland, where it has been clearly demonstrated that shale oil can live against petroleum.

The beds of oil shale in New Brunswick are more extensive than those of any other country, and the by-product obtained on retorting, ammonium sulphate, which was not recovered in the early days, will more than bear the expense of mining and treatment. It is one of the difficulties of a petroleum field that it is almost impossible to estimate the quantity of oil which may exist, and only the successful sinking of wells year by year can show the probable extent of the payable area. The crude oil obtained by retorting New Brunswick oil shale is essentially the same as the petroleum of the mid-continent field, and therefore the same markets are open for it. As an article of commerce, however, it is especially suitable for liquid fuel, and at the present time, as is well known, it has been impossible to secure adequate supplies of liquid fuel for general employment.

College of the City of New York

THE MANUFACTURE OF ANHYDROUS CHLORIN FROM MOIST DILUTE GASES AND ITS INDUSTRIAL APPLICATION IN CHLORIN DETINNING.[1]

By Elmer A. Sperry

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As is well known there are several reactions and operations which produce chlorin, either as a direct or as a secondary product. The uses of this material are also gradually extending and new uses are

[1] Read before the New York Section, American Chemical Society, March 5, 1909.

being developed, for instance, the recently perfected process of chlorin detinning. The supply of chlorin has now outstripped the demand for bleaching-powder, which for years has been almost the sole vehicle for transport of chlorin from the manufacturer to the consumer. Liquid chlorin at once affords a base of supply and provides means of transportation for this valuable material which are unequaled.

The important function that refrigeration can be made to fulfil, in connection with the dehydration and liquefaction of chlorin, constitutes one of the subjects before us.

Since the advent of cheap electrical energy the most abundant source of chlorin supply is the electrolysis of chlorids. The element here is produced as a gas, almost invariably diluted with moisture, vapors and other gases or atmospheric air, or all of these combined.

For the highest economy and efficiency in the process of liquefaction it is desirable to separate the chlorin from the other ingredients and especially moisture. The dry gas representing 100 per cent. chlorin, is the ideal raw material from which to produce liquid chlorin. A moist gas approaching 100 per cent. chlorin may sometimes be had from electrolytic cells running at a high efficiency under conditions of positive pressure. This condition, however, is not one that is thought to be practicable in American practice and with one exception no plant has attempted to put their cells under pressure in this country. The practical considerations seem to be almost insurmountable; not only do the powerfully pungent odors, so poisonous to plant life, persist in and about the plant, but the injurious effects of escaping chlorin are all too keenly evident upon the adjacent landscape. The universal American practice of placing the electrolytic cells under some negative pressure, in case the apparatus springs a leak, or is not absolutely tight, this arrangement results in more or less abnormal dilution of the gas, but under these conditions it is not unusual to meet with chlorin effluent from such apparatus testing between 80 and 90 per cent. chlorin and sometimes higher under conditions of special care.

Considering chlorin, such as last described, it invariably contains moisture in the vicinity of, or even in excess of, saturation at the temperature. Let us now ascertain the effects of the treatment by refrigeration under various conditions as applied for accomplishing certain definite results.

First, the chlorin may be most easily dried by refrigeration under proper conditions, and such moisture as the original gas contains may be caused to combine with the chlorin forming chlorin hydrate which comes down as a solid in the form of snow and is thus separated from the remaining gas, which is now found to have been practically dehydrated. If the dilution factor of dried gas is not too high the direct compression and further refrigeration can be proceeded with at once.

The power factor of liquefaction varies greatly with amount of dilution, very much more power for compression being required in the case of even small dilution, and, furthermore, the gas or diluting gases that are drawn off from the product always contain chlorin to the point of saturation and usually in excess.

Such gases as last described are totally unsuitable to be allowed to escape from the plant, even though a high chimney be employed through which they are ejected, as vegetation in the vicinity of the plant will sooner or later be found to suffer from the chlorin content of these gases.

Refrigeration here serves another excellent purpose accomplishing at the same time two useful purposes: First, the entire saving of all the chlorin and second the removal of the chlorin factor from the gases or air escaping from the plant. This is accomplished by allowing the escaping gases to traverse a small chamber into which is sprayed diluted brine, held at quite a low temperature, in which case the chlorin instantly combines with the water, making more chlorin hydrate, which accumulates and can be handled as a sludge and added to the hydrate originally produced, the sludge being pumped to a chamber leading to the initial or raw chlorin supply pipe, or the raw chlorin may be led over the hydrate, thereby effecting a heat exchange of no little magnitude, again accomplishing two useful results: first, that of pre-chilling the incoming chlorin gas and secondly, the breaking up of the hydrate and liberating the chlorin content as a 100 per cent. gas, which is in this way added to the original incoming supply of raw material raising the percentage of chlorin in quite a marked degree. The thermal units required in breaking up the hydrate, if not furnished in sufficient quantity by the main chlorin supply, are found to be abundantly obtainable in operating another heat exchange by utilizing the warmed brine and utilizing the thermal units represented by the heat of compression on its way to the

liquefying apparatus, thus, at once, cooling the brine and supplying the heat of decomposition of the hydrate.

In the above discussion we have been dealing with chlorin gas in which the gaseous dilution factor is comparatively small. We now turn our attention to the problem of refrigeration in connection with chlorin gas in which the dilution factor is large—too large, in fact, to attempt a compression, even after the most complete dehydration has been effected. Heretofore it has not been commercially possible to employ this raw material for liquefaction. It has been found in practice that gases of almost any dilution can be handled and converted into 100 per cent. chlorin gas and thus practically dehydrated and adapted in every way for liquefaction, all under conditions of high economy. The details of procedure may be varied, but in every instance refrigeration and heat exchange are found to play an important function and are practically indispensable. The process is similar to that described in connection with the effluent gases drawn off from the liquefied diluted chlorin, only conducted on a larger scale, where the entire chlorin content of the diluted moist gases forming the raw material is converted into chlorin hydrate in the presence of the required amount of moisture it is found entirely practicable to abstract this from the diluting brine employed in the form of spray, in connection with and at the time of the refrigeration. Under these conditions by slowing down the velocities it is found entirely practicable to completely separate the chlorin from the diluent, as it will readily be seen that in this instance it becomes a simple matter of separating solids and gases, the solid hydrate from the residuary gases, which are thus allowed to escape at once practically entirely free from chlorin content. The heat exchanges, above mentioned, are now produced for the breaking up of the hydrate and the liberation of 100 per cent. gaseous chlorin, which through the relative vapor tension factors of the hydrate and of water is found to be practically dehydrated as evolved. This, however, is refrigerated once more. There follows from this last step of refrigeration two valuable functions: first, the practically complete dehydration of the 100 per cent. chlorin; second, its thorough pre-chilling prior to compression, which is found in practice to cut down the power factor in the compression steps and do away with the necessity of some of the cooling during this step. The amount of heat evolved in compression of chlorin is not usually understood. As a matter of fact, at 50 lbs. gauge pressure chlorin reaches about 400° C., being 250° hotter than steam at the same pressure, even when cold gaseous chlorin is supplied to the compressor. This serves to illustrate the very great necessity of cooling during, and also just succeeding, compression, and also illustrates the opportunity for the heat exchanges, above described, in connection with the decomposition of the hydrate and the production of the 100 per cent. chlorin from the highly diluted and wet raw material.

There are other features in connection with the liquefaction of chlorin that are interesting, but it has been found that even with 50 per cent. chlorin the work required to be done upon, or the energy represented by, the preliminary stops of refrigeration employing the heat exchanges named, is far less than would be supposed and really can be made to constitute only an insignificant factor in the total cost of liquefaction.

In conclusion, it should be stated that the element of refrigeration, when used in connection with the proper heat exchanges and also utilizing, as has been found entirely practicable, the relative vapor tension factors of the intermediate products, is found to be an extremely economical consideration and to justify the statement that through its aid we are now prepared to commercially liquefy chlorin gas produced under American conditions of negative pressure so that we may expect in the near future the liquid chlorin will be an easily obtainable commodity on the market of this country as it has been for some few years in Germany and we may confidently expect a large expansion in the utilization of this important element in the industries.

The most important of the recently developed uses is doubtless chlorin detinning, most important because probably destined to become one of the largest industrial applications.

In turning to this subject I would state that it was in connection with the development of the system and apparatus known as the Townsend process, beginning in 1901, the writer being especially concerned with the engineering side of this process, abundant quantities of chlorin gas were produced, running very close to 100 per cent. purity, or 100 per cent. chlorin. Endeavors were made to find new uses for this chlorin and among other work the study of reactions between tin and chlorin, especially in the presence of large quantities and surfaces of iron and steel, was under-

taken. Resulting from a close study of these reactions it was discerned almost from the beginning, that special conditions should be provided to render this work commercial, and the reason why some of the results of the eariler experiments above referred to, were not successful, began to be apparent.

In the commercial detinning of tin plate scrap a fourfold object is sought. First, both the tin and steel must be produced in a permanent and thoroughly commercial form. Second, the separation of the tin and steel must be very complete to render the steel valuable. Third, the "black scrap" must be permanently non-rustable, constituting in this way a "weathering" scrap, it being entirely practicable in this way to store the scrap in vast quantities in yards awaiting either changes in the market or availability at the furnace. Fourth, the "black scrap" must be so billeted and compacted as to represent a highly dense material suited to the furnace requirements for melting and also effecting a large saving in handling this otherwise bulky material. A ton of standard tin scrap presents a respectable portion of an acre of superficial surfaces and the processes must be so conducted that the steel will remain unattacked and no loss or deterioration suffered at any step in the procedure.

Preparing the Scrap.—It has been not only suggested, but also the practice in former processes of detinning and even in chlorin detinning to handle the scrap throughout the process in the form of bundles or billets, thus working an obvious saving in the size and investment in plant, as well as labor in and about the plant. I have found that this matter of bundling or billeting can be carried too far for the best results in the various steps of the process. It has been found that for the best results in detinning the compacting should not proceed to the point required to best fit it for the Siemens-Martin furnace. The steel-maker would like the scrap compacted to a point equaling seven to ten cubic inches to the pound, whereas the half to one-quarter of this density for the bundles is much better suited to the process of chlorin detinning. Under these conditions and where the steel-maker is insistent upon the density named a recompacting of the scrap is found to be the simplest expedient. This is a very inexpensive procedure, inasmuch as it consists in delivering to each passing billet on its way to the scrap yard one heavy blow from the steam hammer under conditions of more or less completely retaining the shape of the original billet. For the best and quickest penetration of the billets by the reagent especially where applied in gaseous form the billets should be laminated, *i. e.*, produced by unilinear pressure or pressure in one line or direction only preferably with the lines or planes of cleavage flat-wise of the bundles; this not only facilitates the penetration of the chlorin but aids in removal of the liquid products especially in the steps of the process hereinafter described.

A step of a high degree of importance is the drying of the scrap. Scrap shipped in freight cars apparently perfectly dry will be found to contain from two-thirds to one per cent. of moisture. If shipped in bales or bundles this percentage will run higher than where shipped more loosely. If shipped in open cars the moisture factor will run to 3 or 4 per cent. With chlorin detinning it becomes very essential to render this scrap absolutely anhydrous prior to the reaction period. The reason for this becomes apparent when it is understood that 1 per cent. of moisture is sufficient to convert practically all of the liquid chlorid produced into a solid form, *viz.*, hydrated stannic chlorid, which is difficult to distil or purify and is also extremely adherent to the iron scrap and cannot by any known commercial means be rendered available; the presence of this material causes a very marked loss with both products. One of the aims of the process is to obtain practically all the tin represented on the scrap as anhydrous tetrachlorid, which does not break up on heating to its vaporizing point, but on the contrary readily responds to the ordinary process of distillation for the purpose of purification and separation from other metallic bodies, gases or organic contents.

In my work I have found it more satisfactory to heat the scrap to a point considerably above the boiling point of water just prior to the reaction period, and effect the sealing of the reaction vessel with its full contents of scrap, while the scrap is still hot and before it has had time to again occlude moisture from the atmosphere. Air washing with heated air and opening up the billets of scrap by centrifugal stress are both found to greatly facilitate and hasten the drying step of the process.

The secondary steps of preparation of the scrap need not be named as they have been practiced for years in connection with electrolytic detinning. They consist in treatment with hot alkali for removal of lacquer, comestibles and organic materials, saponifying the greases, etc., etc.

The Reaction Period.—In reacting upon tin scrap with chlorin, liquid tin tetrachlorid at once appears spread over and tends to cover all the surfaces attacked. This layer of chlorid acts as a shield against further attack, reducing the velocity of further reaction inasmuch as the chlorin no longer has free access to the tin surfaces but can only act thereon through the medium of the liquid coating, the chlorid functioning as a chlorin carrier during the further progress of the reaction. Unless removed from the surfaces the presence of the chlorid tends not only to greatly retard the reaction but it decreases the thoroughness with which the tin contained in the "alloy zone" is attacked and removed from the spongy sub-surfaces of the steel plate. Analysis of scrap, where the chlorid is constantly removed from these surfaces during the reaction period, show a decidedly lower value for tin than where the chlorid film is allowed to remain and accumulate on the surfaces. Various means have been suggested for remedying this defect and some have been tested. The one that seems to be simplest and most reliable is to set up a comparatively small centrifugal action in the mass of scrap during the process, which is found to fit the conditions excellently well, owing to the great weight of the chlorid, its specific gravity being about 2.3. Under these conditions the chlorid as fast as generated is thrown away from the surfaces leaving them free for the farther and rapid attack even to the innermost recesses of the *alloy zone*. At the same time the centrifugal stresses are made to serve two other functions of no little interest in connection with this phenomenon. The billets thus being placed under centrifugal stress, especially where so directioned as to coincide with the plane of the laminations of the billet, are found to open up seams and passageways throughout their masses, greatly facilitating the penetration of the chlorin to the innermost portions of the bundles. As a matter of fact 2½ per cent. of the mass of the billets is gradually removed, loosening up the masses causing material changes to take place between the contact surfaces, which is found to greatly hasten the process. Again, the induction and eduction gas passages leading respectively to and from the tall cylindrical reaction vessel are so positioned that a revolving mass within this vessel constitutes a very powerful blast apparatus and the gases are made to rapidly pass through the reaction chamber at high velocity; in at the center at the bottom and out at the periphery near the top, where the heated gases escape to the adjacent vertical cooler through which they pass downwardly out of the bottom of the cooler re-entering the reaction chamber and so are carried round and round with rapidity, accelerating the process in the most marked degree. The reaction between the chlorin and tin generates large quantities of heat and it is one of the prime factors and considerations in designing a detinning plant to so cope with this heat factor that the whole reaction may go forward under commercial conditions as to rapidity, and at the same time under perfect conditions as to heat control.

The temperature must not be allowed to rise above 105° at any point in the reacting mass. The very greatly accelerated circulation, as well as the local perturbation and swirling of the gases throughout, tend to equalize the temperature of the reaction through all the parts of the reacting masses, not allowing one part to reach a higher temperature than another even under conditions of extreme rapidity of reaction and the liberation of enormous quantities of heat. The reaction chamber is water-jacketed and the cooling apparatus standing alongside is not only jacketed but provided with pipes presenting an enormous cooling surface. The rising gases, rapidly heated in the reaction chamber, take up large quantities of the chlorid in the form of vapor, which they instantly give up in descending through the cooler, so that the cooler becomes the largest source of supply of the liquid product. At the same time the scrap throws quite a quantity of liquid against the cylindrical walls of the reaction vessel and thus runs down and joins the effluent liquid from the cooling chamber and escapes to the receptacle through an ordinary sealing trap.

To facilitate these steps the scrap is packed in perforated baskets, set one upon another, surrounding a sturdy shaft which imparts to the baskets a comparatively slow rotatory motion. The shaft is supported from above and simply guided at its lower end.

The change in temperature, or the raising or lowering of the temperature during reaction period is practiced especially at the finish and is found to greatly facilitate the opening up of the scrap for further penetration on the part of the chlorin in finishing, or in fact at any stage of the process. Sometimes this is not necessary, but a slight additional product is usually obtained upon once or twice raising or lowering the temperature of the

masses, showing the probability of a region opened up and reached by the heat changes, which had theretofore failed of penetration. As a matter of fact the temperature is controlled to a degree by admitting the chlorin; a thermometer is placed in the upper eduction passage from the reaction vessel which serves as a means for controlling the whole operation during reaction. The manipulation of the process is found to be very simple and goes forward naturally. By this process several tons of scrap may be thoroughly detinned within the space of from 60–90 minutes with a comparatively small apparatus. Under these conditions last named if no further product is obtained the process is found to be complete and is succeeded by the next step, which is as follows:

Treatment of the Resulting "Black Scrap." A. Removal of Tin Tetrachlorid.—The water from the jackets of the reaction vessel is now turned off and steam up to about 70 lbs. pressure is gradually admitted, the chlorin supply, of course, being cut off. The scrap while still warm is now forced to a heat considerably beyond that of the vaporizing point of anhydrous stannic chlorid, whereupon any chlorid remaining upon or in the scrap is boiled or distilled off and driven out of the apparatus, being carried by the slow revolution of the mass and the slow circulation of the gaseous content, which is given up in the cooler, the gases being returned for further absorption of the chlorid. When the product again ceases to flow from the condenser, valves at the top and bottom of the reaction chamber are so manipulated that hot gases, as originally used for drying the scrap *en suite* in the reaction vessel, are now forced through the scrap and by being drawn from the apparatus through a scrubbing tower, all the tin values that these gases may contain are removed. The black scrap is thus thoroughly air-washed and freed from any remaining tin chlorids, even though they may have become partially hydrated during the reaction process, the air currents playing an important part in distilling and removing the hydrate.

B. Removal of the Iron Chlorid.—The cover of the reaction chamber is now unclamped and the crane handles the heavy shaft with its burden of superimposed baskets, each containing, as they do, a large number of billets of "black scrap." The mass is first raised out of the reaction vessel then lowered while still hot into a washing tank of hot water—here some of the slight film of iron chlorid, which may have been formed during the reaction period, is removed. It is not important to remove all of this material as will presently appear.

C. Ionizing the "Black Scrap."—The masses are now again raised and lowered into a second tank. This second tank contains hot, but rather weak lye, which consists of any solution such as sodium hydrate or carbonate, in which free alkali is present. It is in this tank that a very important part of the process is carried forward and a very necessary quality is imparted to the black scrap, namely, its "weathering" qualities. Billeted black scrap treated as now to be described may be exposed to ordinary weather conditions in an open yard for upwards of a year without serious depreciation. While the scrap is in this tank it is electrolytically treated either with or without agitation or the rotation of the masses of scrap. The current enters the tank from which the main scrap is sufficiently insulated to withstand the extremely low voltage present and passes out through the large central shaft supported and in contact with the baskets of scrap. This constitutes the scrap as the *cathode* and the tank as the *anode*. Under these conditions the acid radical is ionized or broken up and at once seeks the positive pole, or anode, where it simply neutralizes a slight quantity of the alkaline electrolyte, and the hydrogen developed at the cathode exerts to its full its reducing function upon the remaining products reducing them to the metallic state to a degree which is more or less complete depending upon the length of time which the scrap remains under the described conditions in this step of the process. It is usually found that with 300 amperes to the ton about 30 minutes is all that is required for a complete breaking up of the remaining chlorids and the production of the perfectly "weathering" scrap.

The Pre-treatment of the Chlorin.—The same reasons which have been above recited in requiring the scrap to be anhydrous, prior to its treatment by chlorin, will at once be seen to be quite as pertinent and equally applicable to the chlorin itself. Of course, it is well understood that liquid chlorin is thoroughly anhydrous, but this product is considerably more expensive than gaseous chlorin taken directly from the chlorin generating apparatus, and means have been found when desirable for doing away entirely with the necessity of employing liquid chlorin and using the raw chlorin directly from the cells in the present process.

As a matter of fact, in all chlorin processes it is wise to proceed under conditions of sub-at-

mospheric pressure where possible; in this way the works may be maintained sweet and inhabitable, and this point has an important bearing upon the question of labor employed in and about such works. In the use of liquid chlorin there is a constant temptation to allow the gaseous chlorin during the reaction period to increase in pressure above the atmosphere and render the apparatus and connected parts exhalent, so that in case of even minute leakage, operatives are at once seriously affected, as the fumes of anhydrous tin tetrachlorid affect the operatives as seriously even as chlorin itself, so that *the pressure-free* system is to be preferred wherever possible and inasmuch as the positive pressure or the "varying of the pressure" forms no essential feature of this process. It will be seen that the employment of liquefied chlorin is neither important nor necessary.

Considerable expense is also saved. The preparing of the chlorin consists of proceeding under conditions of refrigeration as has already been fully set forth, in connection with the process of liquefaction of dilute chlorin, detailed above.

In addition to refrigeration, it is found that by bringing the dehydrated chlorin into contact with a small quantity of the raw product, tin tetrachlorid, any quantity of moisture still contained in the chlorin, even if minute, is at once "sublimed" and converted into minute isolated particles of hydrated stannic chlorin and circulates and recirculates through the system, being finally carried to the tower as described and the values fully reclaimed in commercial form. When the refrigeration process is carried on, however, under conditions of sufficiently low velocity of gases, the pre-treatment of the chlorin with the chlorid is found unnecessary and the process simply employs the chlorin directly from the cells through the refrigerating apparatus, the excess gases, if any, being constantly passed or sucked through to the tower, the fan beyond the tower also imparting the slight sub-atmospheric pressure so necessary to the entire system.

Preparing the Resulting Chlorid for the Market.—The tin tetrachlorid produced by this process is always yellowish and sometimes a yellowish brown in color, containing, as it does, free chlorin which it has absorbed in the process, and besides, in many instances, some metallic or organic compounds. This product is not suitable for the market and must now be distilled in the usual manner, its specific and latent heat being such as to promote and facilitate this process. With a very little heat exchange the product comes over very rapidly and is perfectly water-white and brilliant. The excess chlorin is returned to the process, the purified product is stored and shipped in steel drums without the necessity of any coating whatever or special treatment of the steel. A steel drum containing one-half ton of this material for the last four years is found to be perfectly free from deterioration and the product uncontaminated.

Handling the Chlorid.—When it is attempted to handle or control the flow of the chlorid in either larger or smaller quantities in either liquid or vaporous form, it is found that valves and cocks, pump-shafts, packing, etc., will tend to cut out and clog, especially where even the thinnest film is allowed to come in contact with the atmosphere. This would not be true if the atmosphere could be guaranteed perfectly free from moisture, but more or less moisture is always present and sooner or later serious trouble is likely to ensue through the formation of the hydrate and consequent "freezing" of the moving part. This is found to be entirely overcome by steam-jacketing these portions. In fact, it has been found that maintaining a temperature above 85° will insure perfect and continuous operation of all of these devices and avoid troubles which are of a serious nature in connection with all such devices. Again, it has been found, where it has been necessary to conduct fumes of tin chlorid, or this material in its vaporous form, especially in the presence of moisture, that the pipes or passages tend to clog by the deposits of the hydrated chlorid upon a cooler wall or surface and finally to entirely stop the duct. To overcome this difficulty, the same jacketing is resorted to and it has been found in practice that lead and other pipes under conditions of jacketing, where the temperature has been maintained approximately at 100° C., have been free from any tendency to clog and when finally examined were found to have retained their original brightness, showing entire absence of any tendency to attack for the period of a year under conditions of the temperature referred to. This is a simple device and one calculated to relieve the operator of many difficulties where attempts are made to handle this peculiar chlorin in the presence of moisture.

Many other operating experiences and conditions of more or less interest might be detailed,

but the present paper has already been extended to a point demanding an apology on the part of the author. It should, however, be remembered that the present art is comparatively new and the difficulties presented and finally overcome are numerous; futhermore, that the practical solution of processes and apparatus suitable for producing this new article of commerce, *anhydrous tin tetrachlorid*, follows from experiences gained through working under commercial conditions to the extent of nearly five tons per day of 24 hours, and naturally cannot be adequately treated in a few paragraphs.

For a more complete understanding of the nature of these difficulties and means developed for overcoming same, reference is respectfully made to the specifications in certain patents given in the foot-note.

REFERENCES.

See U. S. Patents Nos. 382,092, 872,205, 872,092, 873,699, 874,040, 874,707, 875,632, 877,243, 877,244, 877,245, 877,246, 877,247, 877,248, 879,596, 882,354, 883,500, 885,391, 887,538, 897,796, 901,266, 906,321, 877,261, 877,262, 877,263.

Also English Patent No. 25,496, '07, together with the same patents in Germany, France, Belgium and Austria.

Also English Patent No. 8,302, '08, and the same patent in the corresponding countries in addition to Italy, Switzerland and Japan.

THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COKE AND ANTHRACITE.[1]

By Porter W. Shimer.

Received May 12, 1909.

While the standard method[2] for the determination of volatile combustible matter gives useful results on soft coals—for which class it is primarily intended—the results are far too high when applied to coke and anthracite. This is due to oxidation of carbon and, to a lesser extent, to mechanical loss. The atmosphere within the crucible is oxidizing throughout the whole seven minutes' ignition in the case of coke and for perhaps the greater part of the time in the case of anthracite. In the latter case, owing to the decrepitation of this coal when suddenly heated, the mechanical loss may be serious. A number of investigators, among them Meade and Attix,[3] have proposed making this determination in an atmosphere of nitrogen or hydrogen. This, of course, necessitates the use of special apparatus and requires a good deal of time and attention. The results are trustworthy.

For many years, until recently, the writer determined volatile matter on a five-gram sample of coke and anthracite, using a 25 cc. crucible. Before making the ignition a piece of wet asbestos paper was placed over the mouth of the crucible and the closely fitting cover was carefully and firmly pressed down upon it. This made a rather tight joint and the oxidation and mechanical loss were very much lowered. The larger weight of the sample (five grams as against one gram) also lessened the percentage of loss by oxidation.

By a slight modification, however, the standard method may be successfully used. Instead of using a crucible with its cover, the writer now uses two platinum crucibles, without covers, of about 15 cc. capacity each. These are of such a size that, when the smaller one is placed inside the larger one, there will remain an open space at the bottom of about one-quarter inch. The crucibles should be well formed and undented so as to make a close joint, the inner one taking the place of a cover. A porcelain crucible may be used in place of the inner one, if of proper size and cylindrical in shape, but one of platinum is to be preferred.

The method, in brief, is as follows: Ignite the combined crucibles, cool and weigh. Remove the upper one and place it alongside of the other on the balance pan. Weigh into the lower crucible one gram of coke or anthracite. Press the smaller crucible securely down into the lower one and heat for three and a half minutes over the Bunsen and immediately follow this with three and a half minutes over the blast lamp. Simple ignition of seven minutes over the Bunsen, as in the standard method for soft coal, is not enough to drive off all the volatile matter from coke and anthracite. By this double crucible arrangement the interior air space is cut down to a minimum and the joint between the two crucibles is of such a character that very little, if any, air can enter during the ignition. Two more things may be done to minimize still further any possible loss by oxidation. Ten drops of absolute alcohol may be placed on the coke and this may be burned off—in the process expelling the air—by gently and carefully warming the crucibles before beginning the seven minutes' ignition. In most cases, however, this addition of alcohol causes no material difference in the results. A useful precaution to minimize mechanical loss, especially in the case of anthracite, is to work into the joint between the two crucibles a very little stiff starch or flour paste. At the beginning of the

[1] Read before the Lehigh Valley Section of the American Chemical Society, May 6, 1909.

[2] *Jour. Am. Chem. Soc.*, **21**, 1116.

[3] *Ibid.*, **21**, 1137.

ignition this carbonizes instantly and serves to retain the decrepitated particles thrown off in the early part of the ignition. The paste is completely burned away some time before the end of the operation.

In certain cases the crucible containing the coke is more or less attacked, and it is well, therefore, to use a small boat easily made of thin platinum foil, fitting closely into the larger crucible and high enough to contain the sample. A few of the results obtained in this investigation will suffice to show the difference between the two methods of ignition.

A one-gram sample of coke lost in seven minutes' ignition, as in the standard method, with crucible cover, 2.96 per cent. volatile matter. The same sample, when given another seven minutes' ignition in the same way, lost 1.97 per cent. additional.

Using the same Bunsen flame, a one-gram sample of the same coke, ignited for seven minutes in the double crucible, lost 1.20 per cent. and, on giving it an additional seven minutes, the loss was only 0.12 per cent.

To show that all the volatile matter is not driven off by the Bunsen flame alone, the following results, among many similar ones, are given. A one-gram sample of another coke yielded 1.51 per cent. volatile matter by seven minutes' ignition over the Bunsen flame in the double crucible. The sample was again heated for three and one-half minutes over the blast lamp and sustained a further loss of 0.73 per cent. volatile matter. On igniting again for three and one-half minutes over the blast lamp there was no further loss.

It is not necessary to insist on the importance of a fairly accurate determination of volatile matter, for it is not only of value in itself but is essential to the correct determination of fixed carbon.

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RAPID ANALYSIS OF BABBITT METAL.

BY PERCY H. WALKER AND H. A. WHITMAN.

Received May 21, 1909.

Methods for the analysis of alloys of lead, tin, antimony and copper, which are based upon the separation of lead and copper from antimony and tin by the use of alkaline sulphide solutions, are all exceedingly tedious, though with the necessary care, skill and patience, it must be admitted that a method based upon this principle gives results of greater accuracy than any of the more rapid methods. This method is, however, so tedious that it can seldom be used in a commercial laboratory, and when it is used the chances of loss are so great that frequently the whole analysis must be recommenced after spending several days on the tedious separation.

The more rapid methods which are often based upon the separation of antimony and tin by treatment of the alloy with nitric acid are open to the serious objection that one portion of the alloy is used for several determinations and the errors in separation appear again in the determination of the individual metals.

It is highly desirable that we have a method using a separate portion of the alloy for each determination, and that the metal to be determined in each case be dissolved before it is determined. Except for the method of separating copper (and even here Fresenius[1] gives a similar method of separating copper from nickel), there is no new method suggested in the scheme we present. The details of the various determinations have, however, been studied and sources of error in the determination of lead and copper are pointed out, so that by following the method as described and applying the proper correction as accurate results can be obtained as by the alkaline sulphide process in a far shorter time and with much less labor.

THE METHOD.

Copper.—Weigh 1 gram of the alloy into a 250 cc. beaker, add 20 cc. hydrochloric acid and 5 cc. water, heat and complete solution by adding nitric acid in small amounts; with most alloys solution can be effected in a very few minutes and without adding more than 1 or 2 cc. of nitric acid. Evaporate off the acid on a steam bath. It is not necessary to carry to complete dryness, but practically all the acid should be driven off and the residue should be pasty. Add 25 cc. of a solution made of 200 grams tartaric acid, 260 grams of potassium hydroxide, the whole being made up to 500 cc. with water. Heat on the steam bath until solution is completed, add 25 cc. water, boil, add 25 cc. of a 0.2 per cent. invert sugar solution, boil for two minutes, filter through asbestos, wash the precipitate of Cu_2O with water, dissolve in nitric acid, catching the copper solution in a 200 cc. flask, and determine copper by any good volumetric method. We have found that equally good results can be obtained by following Low's iodide

[1] "Quantitative Analysis," Vol. 1, p. 684.

method,[1] or by Jamieson, Levy and Wells' thiocyanate and iodate method.[5] The results are uniformly a little low. This error is not due to volumetric methods employed, both of which give exceedingly accurate results; but nearly 6 per cent. of the copper present is not precipitated as Cu_2O. This loss is uniform for if we add 6 per cent. of the copper determined, the result will be the per cent. of copper in the alloy.

The statement is frequently made that if a Babbitt metal is decomposed by nitric acid, evaporated to dryness, taken up with nitric acid and filtered, that copper can be determined in the filtrate with an error of not more than one or two-tenths of 1 per cent. This is not the case, the error with an alloy containing 5 per cent. of copper will frequently be from 0.5–0.7 per cent. while by the method described above without correction the error will be less than 0.3 per cent., and by applying the correction this error is removed entirely.

Lead.—Dissolve 0.5–1 gram alloy in a 250 cc. beaker as in the determination of copper, when solution is complete, evaporate to dryness on the steam bath, add 5 cc. strong hydrochloric acid (with as much as 10 per cent. Sb use 10 cc. HCl), warm for a few minutes, remove from steam table, add, with stirring, 150 cc. 95 per cent. alcohol, let stand at room temperature for 2 hours, filter on a Gooch crucible, wash with 95 per cent. alcohol, using about 100 cc. Suck as dry as possible, dry crucible in an air bath (one hour at 105° C. is sufficient, though the lead chloride can be heated at 150° with perfect safety). Weigh as $PbCl_2$, add 0.0085 gram to the weight of the precipitate and multiply by 0.74473, the product gives the weight of lead.

The method of separating lead as chloride has been used by several authorities: G. W. Thompson,[3] separates as chloride and then determines as chromate. Olsen,[4] separates and weighs as chloride. Neither of these authors, however, give methods which can give correct results, for the solubility of lead chloride in mixtures of alcohol and hydrochloric acid seems to have been overlooked by both.[5] This may cause errors of several per cent. if the conditions are not made uniform and allowance made for the lead chloride dissolved. The amount of acid present is also of importance. If a large amount of hydrochloric acid is present the liquid will dissolve more lead chloride; if too little acid is present there is danger of precipitating oxychlorides of antimony or tin. We have found, however, that the above proportions of acid and alcohol will cause no precipitation of metals other than lead and will dissolve an amount of lead equal to the correction applied. This holds true for alloys high in lead and for alloys high in tin.

Antimony is best determined by W. H. Low's method[1] which we have slightly modified as follows: To 1 gram alloy in a 450 cc. Erlenmeyer flask, add 10–15 cc. strong sulphuric acid, and heat on hot plate until alloy is thoroughly decomposed. This is generally accomplished in about 30 minutes from the time fumes of SO_3 begin to be given off. Cool, add 200 cc. water and 20 cc. strong hydrochloric acid, boil to make sure that all SO_2 is driven off, cool and titrate rapidly with potassium permanganate which has been standardized against metallic antimony. The true end-point is when a pink color shows after agitating the liquid, though this pink will very soon disappear. The only change we make in the Low method of procedure is to add somewhat less hydrochloric acid. The results are sufficiently accurate for commercial purposes, but the tendency is to get results 0.3–0.4 per cent. high.

Tin is also worked by W. H. Low's method, except that we have found it more satisfactory to use a separate portion of the alloy and reduce with steel turnings instead of with metallic antimony. Treat from 0.2–1 gram of alloy (do not use an amount of alloy containing more than 0.2 gram tin) in a 450 cc. Erlenmeyer flask with 10–15 cc. strong sulphuric acid, heat on the hot plate until the alloy is thoroughly decomposed, cool, add 200 cc. water, 30 cc. strong hydrochloric acid, and about 1 gram of steel turnings, heat and when reduction appears complete, but before the last particles of steel have dissolved, place a two-hole rubber stopper in the neck of the Erlenmeyer flask—one hole of the stopper should carry a tube reaching below the surface of the liquid, the other hole should carry the short arm of a bent tube,

[1] *J. Am. Chem. Soc.*, **24**, 1082 (1902).

[2] *Ibid.*, **30**, 760 (1908).

[3] Stillman, "Engineering Chemistry," 3rd Ed., p. 401.

[4] "Quantitative Analysis," p. 136.

[5] In Thompson's original article, which was published in *J. Soc. Chem. Ind.*, **15**, 179–182 (1896), he states that by using as he does potassium chloride along with hydrochloric acid the amount of lead left in after precipitating as chloride with alcohol amounted to 0.3 per cent. when he was working with solder, and in a private communication since this was written, Dr. Thompson tells us that he makes an allowance for the lead chloride dissolved. He, however, weighs his lead as chromate.

[1] *J. Am. Chem. Soc.*, **29**, 66

the long arm of which reaches nearly to the bottom of a 100 cc. Erlenmeyer flask containing a solution of sodium bicarbonate. This small Erlenmeyer is held on the bent tube by a cork which has a notch cut in it to act as a vent. Through the tube reaching below the surface of the liquid in the large Erlenmeyer pass a current of carbon dioxide, heat to boiling until all steel is dissolved, continue passing CO_2 and cool as quickly as possible; loosen stopper but let current of CO_2 continue, add cautiously some starch solution and titrate with $N/10$ iodine. It is necessary to absolutely exclude air and to standardize the iodine solution with pure tin. Results are accurate.

To test the copper method, amounts of copper, tin, antimony, and lead were weighed out in the proportions of about 4 copper, 13 lead, 8 antimony, and 75 tin, the copper being weighed accurately each time and the copper determined in the mixture as described. The following results were obtained.

Weight of mixed metal. Grams.	Copper taken. Gram.	Copper by titration. Gram.	Copper calculated by taking 106 per cent. of copper by titration. Gram.
1	0.0446	0.0417	0.0442
1	0.0446	0.0422	0.0447
1	0.0446	0.0418	0.0443
2	0.0863	0.0799	0.0847
2	0.0849	0.0803	0.0851
1	0.0407	0.0376	0.0399
1	0.0407	0.0382	0.0405

An alloy, No. 4873, containing 4.66 per cent copper was then taken and the following results obtained:

Weight of alloy taken. Grams.	Per cent. copper by titration.	Per cent. copper by taking 106 per cent. of copper by titration
2	4.35	4.61
2	4.34	4.60
2	4.49	4.75
2	4.42	4.68
2	4.43	4.69
1	4.40	4.66
1	4.37	4.63
1	4.35	4.61
2	4.43	4.70
2	4.39	4.65

Average by proposed method, 4.66. Alloy No. 4873 had been previously analyzed by the alkaline sulphide method with the following results on copper: 4.60, 4.98, 4.37 and 4.68, giving an average of 4.66, the same as by the proposed method. Not only are the determinations carried out by our method much more rapidly than by the alkaline sulphide method, but the individual determinations agree better among themselves.

To test the lead method a similar method was followed, the metals being taken in about the same proportion as for testing the copper determination. Varying amounts of strong hydrochloric acid were used and the following results obtained:

(a) Weight of mixed metals. Grams.	(b) Weight of lead. Gram.	(c) Hydrochloric acid used. cc.	(d) Weight $PbCl_2$ found. Gram.	(e) Weight of $PbCl_2$ + 0.0085 g. Gram.	(f) Per cent. Pb from (e).
2	0.2865	10	0.3649	0.3734	13.60
2	0.2819	10	0.3603	0.3688	13.73
1	0.1418	5	0.1978	0.2063	15.36
1	0.1416	15	0.1818	0.1903	14.17
1	0.1472	25	0.1777	0.1862	13.87
1	0.1489	10	0.1917	0.2002	14.91

These results indicate that better results are obtained when using 1 gram of alloy than when using 2 grams and also indicate that as much as 15 cc. of strong hydrochloric acid could be used without changing the results materially.

The method was then used in determining lead in two alloys with the following results:

Alloy.	(a) Weight of alloy taken. Gram.	(b) Hydrochloric acid used. cc.	(c) Weight of $PbCl_2$ found. Gram.	(d) Weight of $PbCl_2$ + 0.0085 g. Grams	(e) Per cent. lead from (d).	
4874	1	5	0.9924	1.0009	74.57	
4874	1	5	0.9940	1.0025	74.69	
4874	1	10	0.9833	0.9918	73.81	
4874	1	10	0.9857	0.9942	74.07	
4874	1	15	0.9815	0.9900	73.73	
4874	1	15	0.9800	0.9885	73.63	
4873	1	5	0.1683	0.1768	13.17	$PbCl_2$ stood 18 hrs before filtering.
4873	1	5	0.1676	0.1761	13.12	
4873	1	5	0.1661	0.1746	13.01	$PbCl_2$ stood 1 hr. before filtering.
4873	1	5	0.1636	0.1721	12.81	
4873	1	3	0.1706	0.1791	13.34	$PbCl_2$ stood 2 minutes before filtering.
4873	1	2	0.1689	0.1774	13.22	
4873	1	1	0.1705	0.1790	13.33	

The two alloys used had been carefully analyzed by the alkaline sulphide method with a final weighing of lead as sulphate.

No. 4874 gave 74.13 per cent., 74.71 per cent. and 74.44 per cent. lead, averaging 74.43 per cent. lead.

No. 4873 gave 13.34 per cent., 13.28 per cent., 13.07 per cent. and 13.33 per cent. lead, averaging 13.26 per cent. lead.

On alloy 4874 the results obtained by the chloride method, using 15 cc. hydrochloric acid, are somewhat low, and as 10 cc. are enough it is best to use this amount. The last three determinations on alloy 4873 indicate that accurate results can be obtained by using even less than 5 cc. acid and filtering at once.

The methods for tin and antimony are in all essential respects well-known methods, but we have found in the laboratory that they yield good results as the following indicate:

	Antimony by alkaline sulphide method, with final weighing as Sb_2S_3.		Antimony—volumetric.	Tin by alkaline sulphide method with final weighing as SnO_2.	Tin—volumetric.
Alloy	17.28		17 76	7 82	7.98
4874	17.33	17.46	17 90	8 10	7.92
....	17.53		.....	....	....
....	17.68		.. ..	....	....

Alloy	Antimony by alkaline sulphide method, with final weighing as Sb_2S_3		Antimony—volumetric.	Tin by alkaline sulphide method with final weighing as SnO_2.	Tin—volumetric	
....	8.02		8 45	73 98	73 87	
....	7.91		8.38	74.03	75.47	
4873	8.28			.	74 33	
....	7 91	8 03		.	74.42	74 16
....	....		... .	....	73.31	
. ..	....		.. .	.....	74.98	
....	....		....	.....	73 51	

We wish to express our thanks to Mr. F. W. Smither who made the analyses of the two samples of Babbitt metal by the alkaline sulphide method. He used the method described in N. W. Lord's "Notes on Metallurgical Analysis," 2nd Ed. Also to Dr. H. C. McNeil for suggestions on the various methods tried.

[Contribution No. 6 from the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.]

THE THEORY OF FRACTIONAL DISTILLATION.

By Warren K. Lewis.

Received May 4, 1909.

The theory of the separation of a binary liquid mixture into its components coming up for discussion in a seminar conducted by the author in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, it was discovered that but very little work has been done on the subject, and that the results already obtained are incomplete and difficult of access. While qualitatively the phenomena are well understood, methods of calculation of the quantitative efficiency of separation by simple distillation have never been developed, and although separation by rectification has been ably treated mathematically by Hausbrand,[1] still the developments in physical chemistry since the time of his publication enable us to grasp the concepts involved more clearly than was then possible, and thus to develop the formulae more simply, and to carry them somewhat further than he. The general importance of the subject, the entire absence of quantitative treatment of its most important phase, as well as the inaccessibility of Hausbrand's[1] and other pertinent articles,[2] especially to American readers, justify the publication of the methods herein developed.

[1] Hausbrand, "Rectificir- und Distilir-Apparate," Julius Springer, Berlin, 1893.

In the separation by distillation of a binary mixture of miscible liquids, we have, in the terminology of the phase rule, a divariant system. Throughout this discussion we shall make the assumption that the pressure remains constant, inasmuch as most distillations are carried on under atmospheric pressure, and very closely approximate this condition. All our formulae will hold equally well whatever this constant pressure may be, whether below or above atmospheric, and it must also be mentioned that these formulae apply likewise to distillation at constant temperature, the pressure being varied as may be necessary to maintain the equilibrium between the gaseous and liquid phases. If, now, this one external condition (pressure or temperature) imposed upon the system, be kept constant throughout, the effect is the same as reducing it to a mono-variant one. The phase rule, then, tells us that, whichever of the remaining variables we may choose as the independent one, all others are functions

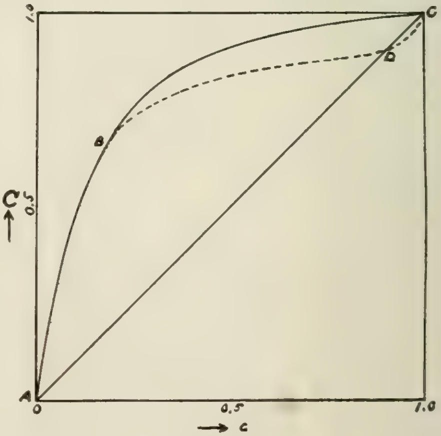

FIG. 1.

of it alone. Since our problem is the separation of a binary mixture into its components, we naturally choose the compositions of the liquid and the gas above it as our variables. At constant pressure (or temperature) the composition of the gas in equilibrium with a given liquid mix-

[1] *Zeitschrift für Spiritusind.*, 1884, 1885, 1896

ture is fixed, and we assume that the composition of the vapor evolved from a given liquid has been experimentally determined for the case to be studied. The methods of making these measurements are to be found in all the ordinary text books on the subject.[1]

Let us define as the composition of a liquid or vapor mixture the fractional part by weight of the more volatile component; thus a liquid or vapor consisting of 40 lbs. of ether and 60 lbs. of carbon tetrachloride would have a composition of 0.40. We will designate the composition of the liquid by c, that of the vapor by C. C is then a function of c alone, and we have assumed this function experimentally measured. These data will be points determining some curve such as A B C (Fig. 1). This curve can, by definition, not start at A below the line A C. It may cross this line farther up, as shown dotted in A B D C. This case we will consider later. If this curve coincides with the line A C, we have

$$C = c;$$

the composition of the vapor is under all conditions the same as that of the liquid and separation by distillation is impossible. This is the case in mixtures of optical isomers.

SIMPLE DISTILLATION.

If a binary mixture of composition c, be put into a still and brought to a boil, it gives off a vapor of composition, C. This vapor is removed as rapidly as formed, and thereby the composition of the liquid, and in consequence that of the vapor as well, are lowered. Let the weight of liquid in the still equal L, and its composition c. The weight of volatile component is cL. If now an amount of liquid dL, of composition C, be boiled off, the composition of the liquid has changed to $c + dc$, where dc is a negative quantity, and it is evident that

$$c + dc = \frac{cL + CdL}{L + dL}.$$

Multiplying out,

$$cL + Ldc + cdL + dcdL = cL + CdL.$$

Discarding differentials of the second order, and solving

$$(C - c)\, dL = Ldc,$$

or

$$\frac{dL}{L} = \frac{dc}{C - c}.$$

$$ln\ \frac{L_2}{L_1} = \int_{c_1}^{c_2} \frac{dc}{C - c}.$$

This equation gives us the ratios of the weights of the liquid in the still for a given composition change. A consideration of the limiting cases involved is interesting. Thus if all the liquid be boiled out of the still, *i. e.*, if $L_2 = 0$, it is evident that since dc cannot give an infinite value to the integral, $C - c$ must become zero; that is to say, all the liquid cannot be boiled out of the still until the compositions of the liquid and vapor phases have become equal; the final composition of the liquid in the still will be represented by the point A in Fig. 1 (by the point C if the original mixture followed the dotted curve and lay between D and C). This equation is not applicable to condensation, owing to our original assumption that the gaseous phase is removed from the system as soon as formed. This is indicated by the fact that the equation becomes indeterminate for $L_1 = 0$. Since we can give finite values to L_1 and L_2, it is clear that dc and $C - c$ can only have zero values simultaneously, *i. e.*, if there be no change in composition of the liquid during distillation, the compositions of liquid and vapor are equal, and conversely. Such would be the point D of Fig. 1. That this is a composition of constant boiling point is proven by the fact already referred to, that the temperature is a function of the concentration alone.

If C can be expressed as a known function of c, this equation is capable of immediate integration and consequent solution. This is possible in the case of certain mixtures, and this solution would be of interest to the mathematical physicist; but inasmuch as these cases are without technical importance, a general graphical solution will be given instead, applicable in all cases where the $c - C$ curves have been experimentally determined, and accurate well within the experimental error of the data. If c be made the abscissae, and the corresponding values of $\frac{1}{C - c}$ the ordinates of a plot, the area under the curve obtained, between the ordinates c_2 and c_1 is equal to the integral desired. This curve is shown for the case of alcohol-water mixtures in Fig. 2. The data are from Gröning's tables.[1]

The usefulness of this curve can best be shown

[1] See Young, "Fractional Distillation," Macmillan & Co.

[1] *Handb. d. Spiritusfab.*, Maercker, p. 626.

by a concrete example. Let us assume that we have a 50 per cent. alcohol (by weight), and we wish to know what percentage distillate we shall obtain if we distil this mixture, in a simple still,

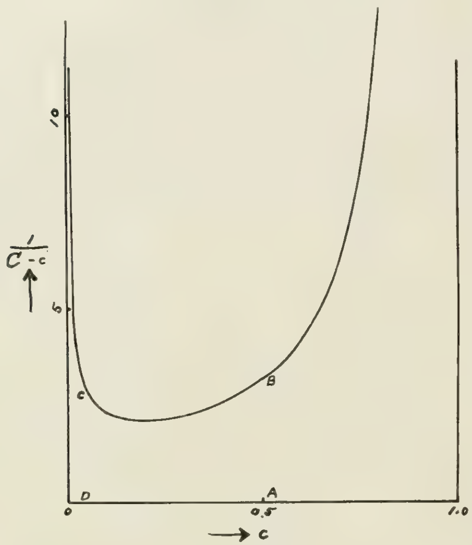

Fig. 2.

till the liquid residue in the still is 5 per cent. The area ABCD, measured with a planimeter, is found equal to 1.075. To this a minus sign must be prefixed as the increment in c is negative. Hence

$$ln \frac{L_2}{L_1} = -1.075.$$

If we start with one pound, $L_1 = 1$, and

$$ln\ L_2 = -1.075$$
$$L_2 = 0.3413 \text{ lb.}$$

We have, then, left in our still 0.3413 lb. of mixture containing 0.0171 lb. of alcohol and 0.3242 lb. water. Since we started with 0.5 lb. of each, our distillate must contain the difference, *i. e.*, 0.4829 lb. alcohol and 0.1758 lb. water or 0.6587 lb. of a 73.3 per cent. alcohol. In this way we can find the separation obtainable in this or any other case, starting and ending with any desired composition in the still, if the $C - c$ curve be known.

While this method suffices both theoretically and practically to solve all problems as to the separation obtainable by simple distillation, still if these problems arise frequently and must be solved rapidly, the use of the planimeter is somewhat disadvantageous. In this case, however, a plot may be made embodying the results of preliminary calculations and suitable for future reference. Assume that we start with a 50 per cent. alcohol in the still. The vapor arising from this is 81.7 per cent., but only an infinitesimal amount of this vapor can be collected, the residue remaining practically 50 per cent. We have already shown that if the residue be boiled down to 5 per cent., the distillate is 73.3 per cent., while if the alcohol be entirely expelled, there is no residue in the still, and the distillate is 50 per cent. Between these extremes still other points may be calculated, and a curve drawn as is done in Fig. 3. Such curves have been indicated for an original charge of 10, 30, 50, and 70 per cent. Thus for a charge of 10 per cent., distilled till the residue in the still is 2.5 per cent., we read directly from the curve that the composition of the distillate is 0.432, *i. e.*, 43.2 per cent. alcohol. These curves may be calculated and plotted as closely together as necessary, and interpolated for intermediate values.

If the amount of distillate be likewise desired, it may be obtained from the readings of these curves with great ease. Thus the curve tells us that a 10 per cent. alcohol distilled to a residue of 2.5 per cent. yields a distillate of 43.2 per cent. Assume the charge one unit by weight, say one pound. The distillate is x lbs. The alcohol in the charge must be equal to that in the residue plus that in the distillate, *i. e.*,

$$0.10 = 0.025(1 - x) + 0.432x$$
$$x = 0.184 \text{ lb.}$$

A 10 per cent. alcohol separates on distillation giving 0.184 lb. of 43.2 per cent. distillate and 0.816 lb. of 2.5 residue per pound of charge.

Our considerations, so far, have been purely theoretical. Let us now consider the disturbances that enter into the operation. These will fall under three heads, superheating, chilling of the vapor, and priming. Local superheating in the liquid can introduce no serious disturbances. The mixture is so agitated by the ebullition that the composition differences at various points cannot be great and cannot long persist. Even though ebullition be excessive at isolated points, the vapor evolved must of necessity have the equilibrium composition, required by our equations. Superheating of the upper part of the still cannot change the composition of the escaping vapors, and hence

cannot affect the separation, though it would involve a waste of heat.

Not so with chilling of the vapors. If the vapors be cooled they partially condense, depositing their equilibrium liquid, thereby enriching themselves. The condensate runs back into the still, to be boiled over again. This phenomenon will be treated under condensation, but it may be noted here that devices intended to increase the efficiency of separation by preventing superheating of the

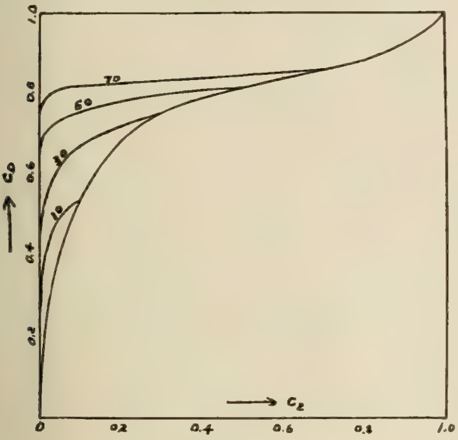

Fig. 3.

upper part of the still always depend on chilling of the vapors to attain their end, ignoring the increased heat consumption involved in the re-evaporation of the partial condensate.[1]

A vapor escaping from a liquid always carries a certain amount of that liquid with it in mechanical suspension. This suspended liquid is known as priming, and the amount of it depends on the rate of ebullition and the nature (viscosity, etc.) of the liquid. Borrowing a term from the steam engineer, let us call the fractional part of the total vapor which is true vapor the "condition" of the same; thus if a mixture is 95 per cent. vapor and 5 per cent. suspended liquid, its condition is 0.95. It is evident that the suspended liquid must be of the equilibrium composition, since it was swept out of such a liquid and has no tendency to change. Our original equation for the change of composition with the loss in weight on distillation becomes

$$c + dc = \frac{cL + xCdL + (1 - x)cdL}{L + dL},$$

or

$$cL + Ldc + dcdL + dcL = cL + xCdL + dcL - xcdL,$$

whence,

$$Ldc = (C - c)xdL$$

$$\frac{dL}{L} = \frac{dc}{x(C - c)}$$

$$ln\frac{L_2}{L_1} = \int_{c_1}^{c_2}\frac{dc}{x(C - c)}$$

In general this equation cannot be integrated, graphically or otherwise, unless x be known as a function of c. In a mixture like glycerine and water, where the one component is exceedingly viscous, x would perhaps be roughly proportional to the glycerine concentration, but in a mixture where the viscosities of the two liquids are not widely different, such as benzol-carbontetrachloride, alcohol-ether, alcohol-water, etc., it is probably safe to assume that the condition is a function of the rate of ebullition alone, and would be practically constant during a given distillation. In this case our equation becomes

$$ln\frac{L_2}{L_1} = \frac{1}{x}\int_{c_1}^{c_2}\frac{dc}{C - c}.$$

The graphical evaluation of the integral, by means of the curve of Fig. 2, makes the solution of this equation at once possible, enabling one to calculate the decrease in efficiency due to priming.

If we have the curves of Fig. 3, we have already shown how $\frac{L_2}{L_1}$ can be calculated by their use for any desired c_1 and c_2. The logarithm of this ratio is, however, the value of the integral required, between the indicated limits, for the case $x = 1.0$. In this way the integral can be determined, and introduced into the above equation, thus solving it without the use of a planimeter.

A word as to the experimental determination of the condition will not be out of place. If the temperature and pressure be measured, the composition of both phases in the mixture can be obtained directly from the tables. The measurement of one other factor dependent for its value on the relative amounts of these phases suffices to determine x. Thus the heat content may be measured by the use of a throttling calorimeter, expanding the vapor adiabatically till superheated, and finding the resultant condition. Another method

[1] See *Jour. Am. Chem. Soc.*, **30**, 1282.

would be to condense the whole mixture and find the composition of the condensate. If a mixture of liquid and vapor is at a temperature, t, and pressure, p, empirical tables give us the compositions of the phases, c and C.[1] Per unit of weight there are x parts of vapor and $1 - x$ of liquid. The composition of the whole is then,

$$xC + (1 - x)c = r.$$

If r be measured, we have

$$x = \frac{r - c}{C - c}.$$

To determine r, and thereby x, a small portion only of the vapor need be tapped off, condensed, and analyzed.

The equations we have developed suggest a new method of at least theoretical interest for determining the $C - c$ curve. If a measured amount, L_1, of a liquid mixture of known composition, c_1, be distilled, the final weight, L_2, and composition, c_2, be found, then the natural logarithm of $\frac{L_2}{L_1}$ is the value of the

$$\int_{c_1}^{c_2} \frac{dc}{C - c}.$$

Let

$$ln \frac{L_2}{L_1} = A.$$

If various values of L_2, and the corresponding c_2 be determined, and the $A - c_2$ curve be drawn, then the tangent to this curve at any point, c, is the value of $\frac{1}{C - c}$ at that point. The tangent may be determined graphically or empirically and the value of C calculated. The usual precautions to prevent partial condensation, etc., would, of course, be necessary.

PARTIAL CONDENSATION.

In the ultimate analysis the only method of increasing the composition of a vapor, that is, enriching it in the more volatile component, is partial condensation. This may be direct, with or without the aid of a rectifying column, or total, followed by a partial revaporization (redistillation). Redistillation evidently involves the greater heat consumption, and hence the importance of the other process.

There are theoretically two different ways of producing a partial condensation, that form two limiting cases between which all actual condensations lie. The first, which we have chosen to call simple condensation, is characterized by keeping the condensate in contact and equilibrium with the residual gas, till the partial condensation is complete. The second, differential condensation, consists in removing the condensate from the system, as soon as formed. Continuous simple condensation may be perfectly and easily realized by maintaining a certain amount of liquid condensate in the condenser, bubbling the incoming vapors through that liquid, securing the partial condensation by cooling the liquid itself, and removing the excess of liquid formed by a continuous overflow at the surface where the vapors escape. We have no mechanical device to accomplish a perfect differential separation, though this is the end at which condenser design must aim.

If we have a weight of gas, G_1, of composition C_1, and wish to enrich it by simple condensation to a composition, C_2, we know that the condensate must have a composition, c_2, connected with C_2 by the curve of Fig. 1. Let the residual weight of gas be G_2. Equating the original and final amounts of volatile component,

$$C_1G_1 = C_2G_2 + c_2(G_1 - G_2),$$

or

$$G_2 = G_1 \frac{C_1 - c_2}{C_2 - c_2}.$$

Since neither G_2 nor $C_2 - c_2$ can be negative, this equation loses its physical significance if c_2 be greater than C_1; in other words the limit of enrichment of a vapor by simple condensation is that vapor which is in equilibrium with a liquid of the composition of the original vapor, while the yield of enriched vapor is in this limiting case infinitesimal.

If the condensation be a differential one, we know that the new composition of the gas is equal to the new amount of volatile component in the same, divided by its total weight, *i. e.*,

$$C + dC = \frac{CG + cdG}{G + dG},$$

whence,

$$CG + GdC + CdG + dCdG = CG + cdG.$$

Discarding the differential of the second order and solving,

$$\frac{dG}{G} = \frac{dC}{c - C}.$$

[1] If the composition, c of the liquid in the still be known, C may be read directly from the curve, Fig. 1, or the corresponding tables.

$$ln \frac{G_2}{G_1} = -\int_{C_1}^{C_2} \frac{dC}{C - c},$$

$$G_2 = G_1 e^{-\int_{C_1}^{C_2} \frac{dC}{C - c}}.$$

Since $C - c$ is always positive, G_2 can become infinitesimal only when $C - c$ becomes zero, *i. e.*, when the composition of the vapor has reached the point C (or D, as the case may be) of Fig. 1.

A differential condensation may be shown to be more efficient than a simple between the same limits, as follows: From the nature of the case we know,

$$c < c_2 < C$$

except for limiting cases when they may become equal. Hence,

$$C - c > C - c_2,$$

$$\frac{1}{C - c} < \frac{1}{C - c_2},$$

$$\int_{C_1}^{C_2} \frac{dC}{C - c} < \int_{C_1}^{C_2} \frac{dC}{C - c_2} = ln \frac{C_2 - c_2}{C_1 - c_2},$$

$$e^{\int_{C_1}^{C_2} \frac{dC}{C - c}} < \frac{C_2 - c_2}{C_1 - c_2}, \text{ or}$$

$$e^{-\int_{C_1}^{C_2} \frac{dC}{C - c}} > \frac{C_1 - c_2}{C_2 - c_2}.$$

Therefore,

$$G_2(\text{dif.}) = G_1 e^{-\int_{C_1}^{C_2} \frac{dC}{C - c}} > G_2(\text{sim.}) = G_1 \frac{C_1 - c_2}{C_2 - c_2}.$$

Hence a differential condensation is more efficient than one, or any number of successive finite, simple, condensations between the same limits, represents the theoretical maximum of efficiency of separation, and may be considered an infinite series of infinitesimal simple condensations. The performance of a condenser should always be given in per cent. of this theoretical maximum, which may be determined by measuring the area under the curve of Fig. 4 (for alcohol-water).

Let us suppose that we require an 85 per cent. distillate from a 20 per cent. alcohol. The still yields us a vapor of 67.7 per cent. We have, then, $C_1 = 0.677$, $C_2 = 0.85$ and $c_2 = 0.657$ (from the $c - C$ curve). A simple condensation yields us then 10.4 per cent. of the original weight of vapor. To calculate the yield of a differential separation, we find the area under the curve of Fig. 4, between the ordinates 0.85 and 0.677 to be 0.458. Hence,

$$ln \frac{G_2}{G_1} = -0.458,$$

$$\frac{G_2}{G_1} = 0.623;$$

i. e., the yield is 62.3 per cent. of the original vapor, obtained as 85 per cent. mixture. A simple condensation in this case has an efficiency of only

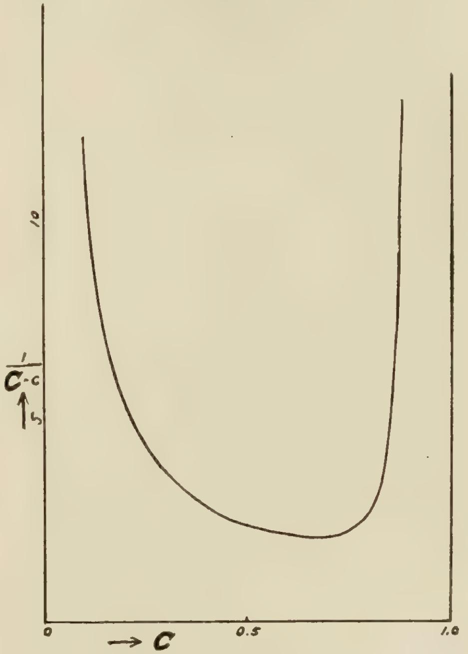

FIG. 4

16.7 per cent. of the best achievable. If instead of one simple condensation we use three, enriching the vapor successively to 74, 80, and 85 per cent., we obtain a yield of 85 per cent. alcohol equal to 52.2 per cent. of the original weight of vapor, *i. e.*, an efficiency of 84 per cent. One readily sees where the efficiency of the ordinary laboratory types of still head has its origin, and how the efficiency of a given type can be very closely

estimated. But of infinitely more importance is the application of this method of calculation to the study of the performance of technical condensers, and to the problem of their improvement and perfection, which is being taken up by this laboratory. The thing to strive for in condenser design is the removal by suitable mechanical devices of the condensate from the vapor as rapidly as possible after formation, and the success with which this ideal is approached is measured by the efficiency of the condenser, calculated as shown.

INTERMITTENT RECTIFICATION.

We assume a still containing the charge, surmounted by a plate tower of the usual type, above which is a partial condenser, the condensate returning to the tower, and the residual vapor passing out to a total condenser to form the required product. For our theoretical discussion we make the following entirely allowable assumptions: (1) that the liquid in the still is great enough in amount so that for a finite time the whole apparatus may be considered as acting as though a vapor of constant composition were indefinitely fed into the bottom of the tower; (2) that the rate of flow at all points in the apparatus is constant, thus producing a stationary condition; and (3) that there is no priming of the vapors.

We shall designate by V the weight of vapor passing through a given section of the apparatus in a unit of time; by C the composition of this vapor; by O the weight of liquid passing the section in the same time; and by c the composition of this liquid. The plate from which this liquid or vapor comes will be indicated by subscripts; thus through a section above the liquid in the still and below the lowest plate passes a rising vapor, V_o, of composition C_o, coming from the charge in the still of composition c_o; and a returning overflow, O_1, composition c_1, from the first plate. Through a section above the n^{-th} plate rises a vapor, V_n, composition C_n, and falls a liquid, O_{n+1}, composition c_{n+1}, from the plate directly above. There are p plates in the tower, and on to the p^{-th} plate flows the condensate, O_c, c_c, from the condenser; and from the condenser passes the distillate V_c, C_c. The heat required to form the vapor, V, from its equilibrium liquid (of indefinite amount) at the boiling point, is K.

Consider the whole apparatus above a section between the n^{-th} and $n+1^{-th}$ plate. There is entering this part of the system only the vapor V_n, from the plate below. There is leaving it the distillate V_c, and the overflow O_{n+1}. According to assumption (2) these must be equal:

$$V_n = V_c + O_{n+1}. \qquad (1)$$

The amount of volatile component entering and leaving must likewise be the same, or

$$C_n V_n = C_c V_c + c_{n-1} O_{n+1}. \qquad (2)$$

Applied to a section just below the first plate these equations become

$$V_o = V_c + O_1, \qquad (1a)$$

and

$$C_o V_o = C_c V_c + c_1 O_1. \qquad (2a)$$

Solving these last two equations simultaneously gives us,

$$c_1 = C_o - \frac{V_c}{O_1}(C_c - C_o). \qquad (2b)$$

It is required of a rectifier to take a charge of a definite composition and yield a definite distillate, at a specified rate. We may then consider C_o and V_c as known from the nature of the problem presented. In other words, the composition of the overflow back into the still is a function of the amount of that overflow alone. This composition, c_1, cannot exceed the value C_o, because the liquid formed by partial condensation is always lower in composition than the vapor from which it is formed, and the two compositions can only be equal in the limiting case of total condensation, *i. e.*, O_1 infinitely great. c_1 cannot be less than c_o since then the vapor above the first plate would be lower in composition than that leaving the still, *i. e.*, our separation would be a negative one. We have then,

$$c_o < c_1 < C_o.$$

Equation (2*b*) transformed gives us

$$O_1 = \frac{V_c(C_c - C_o)}{C_o - c_1},$$

whence

$$\frac{dO_1}{dc_1} = \frac{V_c(C_c - C_o)}{(C_o - c_1)^2}.$$

Since our tower gives us a separation of the components, $C_c > C_o$, and hence this differential coefficient is positive, increasing in value with increasing c_1, it is evident that O_1 is a minimum when c_1 has its lowest possible value, *i. e.*, when $c_1 = c_o$. Since from equation (1) the less the overflow, O_1, the greater V_c for a given V_o, the maximum efficiency is obtained from a tower when $c_1 = c_o$.

It might be suggested that this is not of necessity a point of maximum heat efficiency if one component of high heat of vaporization should decrease in the overflow, but be overbalanced by a greater increase in the second component of very low heat of vaporization. That both components increase is shown, however, by the fact that

$$\frac{d(1 - c_1)O_1}{dc_1} = (1 - C_o)\frac{V_c(C_c - C_o)}{(C_o - c_1)^2},$$

and

$$\frac{d(c_1 O_1)}{dc_1} = C_o \frac{V_c(C_c - C_o)}{(C_o - c_1)^2},$$

both positive quantities. These equations only say what is self-evident, that the only way to increase the overflow is to boil up more vapor out of the still and completely condense this increase.

This argument may be applied with equal validity to equations (1) and (2), and so we may say that a tower is working at its maximum efficiency only when the compositions of the liquids on succeeding plates do not differ more than differentially. But in this case the vapors rising from them and in equilibrium with them can likewise differ only differentially; to obtain a finite separation at maximum efficiency requires an infinite number of plates.

These equations enable us to calculate directly the performance of a theoretically perfect rectifier, for any desired separation, namely by making $c_1 = c_o$ in equation (2*b*) and solving for O_1. Substituted in (1*a*) this gives us,

$$V_o = V_c\left[1 + \frac{C_c - C_o}{C_o - c_o}\right]$$

$$= V_c\frac{C_c - c_o}{C_o - c_o}. \qquad (1b)$$

If a rectifier receive a charge of composition c_o, and yield a distillate, C_c, the theoretical maximum of efficiency is $\frac{C_o - c_o}{C_c - c_o}$ pounds of distillate recovered per pound of vapor boiled out of the still. If K_o be the heat of vaporization of the vapor issuing from the still, the heat consumption per pound of distillate would be $K_o\frac{C_c - C_o}{C_o - c_o}$ B. T. U., not allowing for bringing the liquid up to the boiling point.

If we can measure the actual composition of the overflow into the still of an apparatus in operation, by the insertion of a thermometer into the liquid on the first plate, by removing a sample and analyzing it, or by any other suitable means, we have all the data necessary for calculating the actual working efficiency of the system. The rectifier is yielding $\frac{C_o - c_1}{C_c - c_1}$ pounds of distillate per pound of vapor from the still, whereas a perfect type would yield $\frac{C_o - c_o}{C_c - c_o}$ pounds. The efficiency is equal, then, to $100\frac{(C_o - c_1)(C_c - c_o)}{(C_c - c_1)(C_o - c_o)}$ per cent.

Equations (1) and (2) give us

$$c_{n+1} = C_r - \frac{V_c}{O_{c+1}}(C_c - C_n).$$

In a working column it is essential to have c_{n+1}, for a given C_n, as large as possible, and this is attained by increasing O_{n+1}. We have already shown that the greater O_{n+1}, the greater c_{n+1} and in consequence the greater the rate of separation as we go up the tower. It is desirable, then, to maintain O_{n+1} as great as possible on every plate. If, due to poor insulation, we have partial condensation in the lower part of a column, the overflow thus formed does not pass the upper plates, and in consequence these plates are less efficient than they would be if this condensation took place above them and returned through the whole system. In other words, the more perfect the insulation of the plate tower of a rectifier, the better its performance. The condensate should be entirely formed in the condenser at the top, and return through the entire length of the rectifier.

We see then that in an ideal rectifier the vapors from the still pass up against the counterflow of the partial condensate formed from them in the condenser. As the vapors enter each plate they condense, boiling off with their heat of condensation a new and richer gas mixture from the liquid there, the composition of the vapor above a plate being connected by the c — C curve with the liquid on it. The function of the column is to remove as far as possible, from the condensate of the condenser above, the volatile constituent, returning as a final overflow to the still only the non-volatile plus what volatile cannot be boiled out. Since a differential condensation leaves least volatile component in the liquid it leaves least for the *e* column to perform, and a given tower gives its best performance when the condenser over it is a differential one.

If we consider that part of a rectifying column between two sections, one just below, and one just above the $n^{-\text{th}}$ plate, equating receipts and deliveries,

$$V_{n-1} + O_{n+1} = V_n + O_n, \tag{3}$$

and

$$C_{n-1}V_{n-1} + c_{n+1}O_{n+1} = C_nV_n + c_nO_n, \tag{4}$$

which, applied to the first plate, give

$$V_o + O_2 = V_1 + O_1, \tag{3a}$$

and

$$C_oV_o + c_2O_2 = C_1V_1 + c_1O_1. \tag{4a}$$

Having shown its desirability we now introduce a new assumption, *viz.*, (4) that the walls of the plate column are non-conducting. On to and from each plate are running overflows approximately equal in amount and temperature, and so the quantities of heat brought in and taken out by them are very nearly the same; this must then likewise be true of the heats of the vapors condensing and evolving, *i. e.*,

$$V_1K_1 = V_nK_n = V_{n+1}K_{n+1} = V_mK_m = V_oK_o. \tag{5}$$

This equation is beyond doubt very closely fulfil'ed because these heats of vaporization are so much larger than the corresponding specific heats of the liquids flowing through, that a rather large change in the heat of the liquid would vitiate the above equation but little.

Now given

$$K_n = F(C_n), \tag{6}$$

and

$$C_n = f(c_n), \tag{7}$$

with their special cases,

$$K_1 = F(C_1) \tag{6a}$$

and

$$C_1 = f(c_1), \tag{7a}$$

we have in equations (1*a*), (2*a*), (3*a*), (4*a*), (5), (6*a*), and (7*a*) the known quantities c_o, C_o, V_c, C_c, and K_o, while unknown are V_o, O_1, c_1, O_2, V_1, c_2, C_1, and K_1. With the help of these seven equations, however, we can solve for all these unknowns in terms of any one of them, let us say, V_o. Applying these equations successively to each plate as we go up the tower we can express all unknowns in terms of this same V_o, getting finally,

$$c_c = \phi(V_o), \text{ and } V_p = \psi(V_o).$$

We know, however, that

$$c_c = \theta(V_p, C_c),$$

the nature of the function depending on the method of condensation employed. These three equations enable us to evaluate V_o, and from the point of view of the mathematical physicist our problem is solved. Practically, however, we must proceed somewhat differently.

Applied to the top plate, equations (1) and (2) give

$$O_c = V_p - V_c \tag{1c}$$

and

$$c_cO_c = C_pV_p - C_cV_c. \tag{2c}$$

We know what the apparatus is to deliver, *i. e.*, we know V_c and C_c. Now assume either (1) a simple condensation, in which case c_c is at once known from the c — C curve; or (2) a condensation definitely known from the measured performance of the particular condenser used, giving C_c empirically; or (3) for the ideal case a differential condenser. In either case assume a value for either C_p, V_p or O_c. Under the first two assumptions all these quantities are at once known; under the third, knowing C_p and C_c, c_c can be calculated at once; if V_p or O_c be given, readily by successive approximation.

Equations (3), (4), and (5) give us

$$V_{p-1} + O_c = V_p + O_p, \tag{3c}$$

$$C_{p-1}V_{p-1} + c_cO_c = C_pV_p + c_pO_p, \tag{4c}$$

$$V_pK_p = V_{p-1}K_{p-1}. \tag{5c}$$

We must now introduce our last assumption, which is unfortunately not so valid as our previous ones, namely, that the heat of vaporization of the two components may be considered as constant over the temperature interval involved, and that the heat of vaporization of the mixture equals the sum of that of the components. While this assumption is only an approximation to the function, K = F(C), it is the best we can make at present and in many cases will beyond doubt give very close results. It cannot be used when the heat of mixing of the liquids is large, as in the case of sulfuric acid and water, for example. An exhaustive study of the heats of vaporization of important mixtures must be undertaken. Calling k_a and k_b the heat of vaporization of the components, we have

$$K = k_aC + k_b(1 - C). \tag{6}$$

Knowing C_p we can calculate K_p at once, and write:

$$(5d)\quad V_pK_p = V_{p-1}K_{p-1} = V_{p-1}[k_aC_{p-1} + k_b(1 - C_{p-1})].$$

The equations (3*c*), (4*c*), and (5*d*) contain only three unknowns, V_{p-1}, O_p, and C_{p-1}.

They are solved as follows:

$$O_p = V_{p-1} - V_c = \frac{C_{p-1}V_{p-1} - C_cV_c}{c_p}. \tag{7}$$

$$V_{p-1} = \frac{c_p V_c - C_c V_c}{c_p - C_{p-1}} = \frac{V_p K_p}{k_b + C_{p-1}(k_a - k_b)}. \quad (8)$$

Equation (8) is a simple algebraic containing only C_{p-1} undetermined. C_{p-1} being thus obtained, the $c - C$ curve gives us c_{p-1}. Equation (8), being in its more general form

$$\frac{c_n V_c - C_c V_c}{c_n - C_{n-1}} = \frac{V_p K_p}{k_b + C_{n-1}(k_a - k_b)},$$

can be applied at once to find C_{p-2}, and so on down the still to c_0, below the bottom plate. Equation (8) gives us V_0 and (7) O_1. We have found then the theoretical performance of the given tower, with the assumed condensation. If this condensation were differential, the performance calculated is the theoretically maximum of which the given still is capable. Varying the overflow by assuming other values for the condensation process, we determine as many points as may be necessary on the $c_0 - \frac{V_0}{V_c}$ curve, interpolating for any desired values. For a given column, with a given method of condensation, a series of such $c_0 - \frac{V_0}{V_c}$ curves may be drawn for varying distillates (*i. e.*, varying C_c) and these curves would give at once by substitution in equation (1*a*) and (2*a*) the maximum efficiency for a required operation, of which the apparatus is capable.

The heat consumption q, corresponding to a charge in the still of composition, c_0, and a distillate, C_c, requiring a vaporization from the still of $\frac{V_0}{V_c}$ pounds per pound of distillate obtained is $q = \frac{V_0 K_0}{V_c}$ B. T. U. per lb. distillate, disregarding the heat necessary to raise the liquid in the still to the boiling point. Of this heat consumption

$$\frac{O_c}{V_c}(k_a c_c + k_b(1 - c_c)) = \frac{O_n}{V_c}(k_a c_n + k_b(1 - c_n)) \text{ B. T. U.}$$

are extracted by the cooling water of the partial condenser, while the rest, K_c B. T. U., must be absorbed in the final condenser, plus the amount necessary to cool the distillate to room temperature.

A numerical illustration will most readily make clear the use of these equations. A plate tower, with a differential condenser above, is yielding an 85 per cent. distillate. We assume that the liquor on the top plate is 20 per cent., thus giving off a vapor of 67.7 per cent., which enters the condenser, and is there enriched to 85 per cent. Assume a delivery of 100 lbs. 85 per cent. alcohol per unit of time. We have already shown under condensation that in this case each 100 lbs. of 67.7 per cent. vapor entering the condenser yields 63.3 lbs. enriched product and a condensate of 36.7 lbs. of 37.9 per cent. alcohol. Hence we have

$$V_c = 100, C_c = 0.85; V_p = 158, C_p = 0.677;$$
$$O_c = 58, c_c = 0.379, c_p = 0.20; k_a = 371, k_b = 979.$$

The equation connecting the composition of the liquid on the n^{-th} plate with that of the vapor entering it

$$\frac{c_p V_c - C_c V_c}{c_p - C_{p-1}} = \frac{V_p K_p}{k_b + C_{p-1}(k_a - k_b)},$$

becomes then for this column under these conditions,

$$979 - 608\, C_{n-1} \quad \frac{89{,}700}{100\, c_n - 85}(c_n - C_{n-1}).$$

Applied to the top plate, where $c_n = 0.20$, this equation gives us $C_{p-1} = 0.633$, as the composition of the vapor rising from the $p-^{1-th}$ plate. The liquid on this plate, c_{p-1}, must be, from the $c - C$ curve for alcohol, $c_{p-1} = 0.158$. Substituting this value, and solving for the $p-2^{-th}$ plate, we obtain $C_{p-2} = 0.621$; hence $c_{p-2} = 0.149$. In exactly the same manner we obtain, $c_{p-3} = 0.148$ and c_{p-4} has practically the same value. In other words, further increasing the length of the tower will not materially improve the separation. Assuming therefore four plates we have $c_{p-4} = c_0$, the liquid in the still. c_1 is so nearly equal to c_0 that, barring inaccuracies involved in our assumptions and the available data, this combination gives us an efficiency of 99 per cent. of the theoretically maximum. This is due to the fact that we assumed a differential condenser, and such figures as these show, more clearly than any algebraic equations can, how much the efficiency of a rectifier depends on the condensation. The perfection of the condenser is the problem of the still designer to-day.

To obtain the heat consumption,

$$O_1 = \frac{V_c(C_c - C_0)}{C_0 - c_1} = \frac{100(0.85 - 0.619)}{0.619 - 0.148} = 49.1,$$

$$V_0 = V_c + O_1 = 149.1,$$

$$q = \frac{V_0 K_0}{V_c} = 897 \text{ B.T.U. per pound of 85 per cent.}$$

distillate produced from 14.8 per cent. "beer."

Let us assume an original charge of composition c_0^0 and weight L in our still, rectified to yield at all

times a distillate, C_c. This is accomplished by gradually increasing the flow of cooling water through the condenser, thus enlarging the overflow O_c, and in consequence the vapor consumption $\frac{V_o}{V_c}$. If this process be carried on till the residue in the still is of a required purity, c^1_o, what has been the total heat consumption, Q, per pound of distillate?

We have shown (1) how for a given still in operation points on the $c_o - \frac{V_o}{V_c}$ curve may be exactly measured; (2) how this same curve may be calculated for a given still working at its theoretical maximum efficiency; and (3) how this curve may be found for the theoretically perfect still. We shall now give the formulae, which, if the values read from the first curve be inserted, will give the actual heat consumption of the operation measured; if from the second curve, the theoretically minimum heat consumption of the still studied; and if from the third, the theoretically minimum amount of heat to give the separation required. If we call these heats Q_1, Q_2, and Q_3 we may consider $\frac{Q_3}{Q_2}$ as the theoretical efficiency of the still in question, $\frac{Q_3}{Q_1}$ as the actual working efficiency of the separation, and $\frac{Q_2}{Q_1}$ as the efficiency of operation of the still.

Calling D the weight of the total distillate obtained when the composition of the residue in the still has reached c_o, we have

$$c_o = \frac{c^o_o L - C_c D}{L - D}, \text{ or}$$

$$D = L\,\frac{c^o_o - c_o}{C_c - c_o}.$$

We know likewise that the heat consumption per pound of distillate at this composition in the still c_o is

$$q = \frac{V_o}{V_c} K_o.$$

By the use of the proper $c_o - \frac{V_o}{V_c}$ curve we can thus calculate for varying values of D the corresponding values of q, and construct a curve with D as abscissae and q as ordinates. The total heat consumption Q is

$$Q = \int_o^{D_s} q\,dD, \quad \text{where}$$

$$D_s = L\,\frac{c^o_o - c^1_o}{C_c - c^1_o}.$$

Q is measured by planimetering the area between the D—q curve, the D axis, and the ordinate D_s. Whether the Q obtained is theoretical or actual depends on the $c_o - \frac{V_o}{V_c}$ curve used to calculate the D—q relationship, as was pointed out in the preceding paragraph.

We have thus solved the problem we set before us, showing how the theoretical working of a rectifier may be calculated and the actual separation measured and followed. To calculate the disturbances due to priming, to poor insulation and resultant local condensation, and to the imperfect establishment of equilibrium would lead us at this time too far, but the methods here outlined can be applied to these problems and are being taken up in this laboratory. The still designer must likewise have data as to the influence of the rate of flow of the vapors through the tower on the rate with which equilibrium between the vapors and the liquids through which they pass is reached. The object of this paper was not to attack these problems, but to develop methods of calculation that would show what data are needed, and prove, we trust, an incentive to experimental work in this so important field of chemical engineering.

CONTINUOUS RECTIFICATION.

While continuous rectification is the most important type of practical distillation, and while the equations for such columns should in a suitable place be published at length, the method of calculation is so entirely similar to that just given, that from our present point of view nothing would be gained by developing them here. We will only outline the scheme to be followed:

The theoretically minimum heat consumption of separation is the same, down to the delivery plate, whether the process be continuous or not and is given by calculating Q_3 as already shown. For a given still, of given delivery, we follow down through the tower exactly as before, except that when we reach the plate upon which the "beer" enters we must change our equations for the new overflow. Thus, we get the theoretical efficiency of the given still.

To calculate the working heat consumption, knowing the composition of the "beer" and distillate we need measure only that of the "slop," exactly as be ore we needed to know only that of the overflow into the still. One point must be mentioned; if the steam be injected into the vapor space above the "slop" we have $C_o = o$; if, as should be done, the vapor for running the tower be obtained by boiling the "slop," either with coils or direct flame, as the case may be, C_o corresponds to the c_o of the "slop."

[CONTRIBUTION FROM THE LABORATORY OF THE HAWAII EXPERIMENT STATION]

MANGANESE IN SOME OF ITS RELATIONS TO THE GROWTH OF PINEAPPLES.

BY W. P. KELLEY.

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For a number of years pineapples have been grown on the upland plains of the Hawaiian Islands. In some of the fields devoted to this crop there are spots varying from one to sometimes more than twenty acres in size on which pineapples do not grow well. On these areas the young plants usually make a fair growth for a few months; but then the leaves begin to show a reddish purple color, which soon gives place to a yellowish white appearance, which color persists throughout the remaining life of the plant. Many such plants never bear fruit; that which is produced, however, is always inferior in size and quality. The areas thus affecting this crop are quite definite and with the rapid expansion of the pineapple industry in recent years, such soil has been found to be much greater in extent than was formerly thought. All efforts of the best growers, including the applications of fertilizers and lime, good tillage, drainage, etc., have not effectually changed the growth of the pines on these lands.

Practically all the soil of the Hawaiian Islands is of volcanic origin and one of its chief characteristics is its high percentage of iron,[1] which, in many instances, imparts to the soil a brick-red color. The soil on which the pineapples become yellow, however, is usually dark in color, sometimes almost black. From this difference in color, it is common in Hawaii to speak of pineapple soils as being red or black, meaning thereby good or poor pineapple land; and it is in this sense that the terms red and black soils are used in this paper. In addition to this difference in color, the black soils appear to have a finer texture than the red soils. When reasonably dry and in good tilth, the red soil usually has a granular or "shotty" texture, while the black soil, under similar conditions, is reduced to a finer state of division. Upon thorough wetting, however, either of these types[1] may be crushed between the fingers to such a fine state of division that practically all of it will pass through a one-hundred mesh sieve. There is, therefore, very little true grit in this section, a very complete disintegration of the lava having taken place, which, in some localities, extends to a depth of thirty feet or more.

In consideration of the extent of the black soil and its unusual character, the Hawaii Experiment Station has undertaken an extended investigation of the question. This work is still in progress, but it is thought that results of sufficient importance and scientific interest have been obtained to justify their publication at this time. This paper should, therefore, be regarded as a preliminary report, rather than a complete discussion of the subject.

In September, 1908, two extensive series of fertilizer plot experiments were begun: one on red soil, and one on black. There was a twofold object in these experiments: first, to determine the fertilizer requirements of pineapples in Hawaii; second, to ascertain the cause of pineapple yellowing on the black soil. This paper deals with the latter of these only.

At the beginning of these experiments, a number of samples of soil and sub-soil were taken from various parts of the pineapple district. About one-half of these samples were from the black soil, where the pines were very yellow; and one-half from red soil, producing good pines. The samples of soil were taken to a depth of eight inches; and the sub-soil from eight to twenty inches below the surface. Each of these samples represents a composite, taken from not less than six different places; and, therefore, the average of the six samples of each type may be looked upon as representing not less than thirty-six different places in the red and black soils, respectively. In the following table is given the average water-free composition of the two types as determined by the methods of The Association of Official Agricultural Chemists.

[1] See "Lavas and Soils of the Hawaiian Island" by Maxwell.

[1] The word "type" is not used in this paper in its usual sense, but rather for the sake of brevity.

TABLE I

Average composition of:	Red soil. Per cent.	Red sub-soil. Per cent.	Black soil. Per cent.	Black sub-soil. Per cent.
Insoluble matter	42.82	41.42	35.26	37.73
Potash (K_2O)	0.59	0.63	0.91	0.87
Soda (Na_2O)	0.27	0.25	0.31	0.41
Lime (CaO)	0.36	0.48	0.97	0.58
Magnesia (MgO)	0.39	0.38	0.47	0.41
Manganese oxide (Mn_3O_4)	0.37	0.20	5.61	4.90
Ferric oxide (Fe_2O_3)	27.82	30.10	22.58	22.96
Alumina (Al_2O_3)	10.04	10.37	15.39	17.20
Phosphorus pentoxide (P_2O_5)	0.08	0.12	0.27	0.16
Sulphur trioxide (SO_3)	0.11	0.08	0.17	0.06
Volatile matter	15.14	13.74	17.61	13.67
Titanium oxide (TiO_2)	2.01	2.49	0.88	1.08
Total	100.03	100.26	100.43	100.03
Nitrogen (N)	0.32	0.24	0.37	0.20
Acidity[1]	1235.0	......	98.0	......

The pineapple growers in Hawaii often refer to their black soils as being "sour," and many of them are inclined to attribute the yellow, dwarfed appearance of the plants on this land to this cause. In this connection, investigators elsewhere have pointed out that the pineapple plant is very sensitive to acidity.[2] But in view of the fact that the determination of acidity in these soils shows the presence of much less actual acidity in the black soil than in the red soils (see table above), it seems that, considering this factor only, the black soils should be the more productive of the two. In fact, every sample of the black soil analyzed contained less acidity than any of the red soils, and furthermore, some of the black soils were found to be neutral. It, therefore, seems reasonable that some cause other than acidity is bringing about the unfavorable growth. By reference to the table, the black soils are shown to contain even more of the so-called plant foods than the red soil, and in this connection, it is especially noteworthy to point out that the black soil is well supplied with nitrogen, phosphoric acid and potash.

It is well-known, however, that the usual chemical analysis of a soil is not sufficient to determine its crop-producing power; that the chemist often fails to recognize certain conditions in the soil, which have great influence on crops; and further, that the usual chemical analysis fails to indicate the availability of the elements in the soil; but without discussing this subject further, it is sufficient at this time to say that the application of liberal amounts of various high-grade fertilizers, in conjunction with good tillage, drainage, etc., has not resulted in overcoming the yellowing of the pines on this land. The plots of black soil, to which nitrogen, phosphorus, potassium and calcium, in various forms and amounts, have been applied, do not indicate an effectual remedy for the yellow, stunted growth of pines there. Some of the same applications to red soil, on the other hand, are proving highly satisfactory. What then is the cause of this phenomenon?

[1] Calculated to pounds of CaO per acre foot.

[2] *Bull* **68**, *Florida Experiment Station*, page 697.

By again referring to the previous table, one striking difference in the composition of the two types is apparent, namely, in their manganese content. In order to bring out this point more forcibly, the following table is submitted, which shows the complete analysis of the soils containing the maximum, minimum and average percentages of manganese oxide as found in each type.

TABLE II

	Black soils.			Red soils.		
	Max. Per cent.	Aver. Per cent.	Min. Per cent.	Max. Per cent.	Aver. Per cent.	Min. Per cent.
Insoluble matter	33.45	35.26	34.86	39.07	42.85	44.00
Potash (K_2O)	0.83	0.91	1.06	0.76	0.59	0.59
Soda (Na_2O)	0.40	0.31	0.29	0.33	0.27	0.29
Lime (CaO)	1.39	0.97	0.36	0.29	0.36	0.24
Magnesia (MgO)	0.54	0.47	0.40	0.35	0.39	0.41
Manganese oxide (Mn_3O_4)	9.74	5.61	3.91	0.91	0.37	0.15
Ferric oxide (Fe_2O_3)	19.65	22.58	26.39	24.98	27.62	27.94
Alumina (Al_2O_3)	15.50	15.39	14.85	14.73	10.04	11.91
Phosphorus pentoxide (P_2O_5)	0.21	0.27	0.18	0.10	0.08	0.03
Sulphur trioxide (SO_3)	0.16	0.17	0.13	0.17	0.11	0.11
Volatile matter	17.73	17.61	16.33	17.84	15.14	13.94
Titanium oxide (TiO_2)	0.73	0.88	1.54	0.23	2.01	0.28
Total	100.33	100.43	100.30	99.76	100.03	99.89
Nitrogen	0.39	0.37	0.30	0.34	0.32	0.29

Since the above analyses were made, numerous other samples have been drawn, both from red and black soils; and in every instance, the samples drawn from sections where the pines are yellow, have been found to contain large amounts of manganese, whereas, those taken from the red soil, on which thrifty pines grow, contain little of this element. In general, the black soils contain from ten to fifty times as much manganese as the red soils.[1]

All the samples previously referred to were drawn from extremes, that is, either from sections which produce very yellow plants, or from soils producing very thrifty, green pines. The yellow and green areas are not separated by sharp lines of division, however, but rather gradually merge the one into the other. There is, therefore, an inter-

[1] It has been previously pointed out that some Hawaiian soils contain large amounts of manganese (see *Press Bulletin No.* **18**, *Hawaii Experiment Station*), but no effort has been made to correlate yellowing of pineapple with the occurrence of manganese in the soil.

mediate area surrounding the yellow spots on which the pines show the yellowing effect to a lesser degree. With the view of determining whether the manganese likewise decreases in passing from the black soil to the red, several series of samples from different places were drawn at regular distances apart, in passing from the black to the red soil. From the analysis of these samples, a very close correlation between the yellow color of the pineapples and the manganese content of the soil was found to exist.

The following table will show the average percentages of the oxide of manganese in black, intermediate and red soils.

TABLE III.

	Black.	Intermediate.	Red.
Manganese oxide (Mn_3O_4)	5 61	1 36	0 37

It seems, therefore, that some correlation exists between the yellowing of pineapples and the amount of manganese in the soil.

According to LeClerc,[1] manganese is an almost universal constituent of soils, and it is often not determined in soil analyses for the reason that it is not usually regarded as a necessary element of plant food, and is thought to have little or no economic importance in crop production. Among all the soil analyses, to which the author has had access, none have been reported that contain more than a few tenths of 1 per cent. of Mn_3O_4.

The solubility of a substance in the soil, however, determines in a large measure its influence on plant growth. Sodium, for instance, while not usually considered as an essential to plant growth, when present in the form of a soluble salt, is known to exert a marked influence on crops. Wheeler and Hartwell,[2] at the Rhode Island Experiment Station, have shown that soluble sodium compounds may even partially take the place of potassium in the development of certain plants and in certain instances, sodium may perform a physiological function in the development of these plants. The occurrence of large amounts of soluble sodium compounds in the soil, however, is known to be very detrimental to the growth of plants. As is well-known, sodium and potassium are closely related elements and have many properties in common. Manganese and iron are likewise closely related. It has been shown that when certain plants are grown in culture solutions containing very small amounts of iron, the application of a small amount of soluble manganese brings about new vigor and increased chlorophyl production, and in this connection the solubility of the manganese and iron in the black soil becomes a matter of interest. The chief function of iron in plants seems to be connected with the production of chlorophyl, and since the general appearance of the yellow pines indicates that the chlorophyl has been affected, the possibility of some influence on the part of the manganese at once suggests itself. In this connection Loew and Sawa, in commenting on the work of Birner and Lucanus, says: "In regard to the behavior of plants toward manganese compounds, but few experiments have been made and those show that manganese cannot replace the related iron in regard to the production of chlorophyl; and that the manganous and manganic phosphate suspended in culture solutions can exert an injurious effect."[1]

With the view of determining the solubility of the manganese and iron, a number of samples of both red and black soils were extracted with a one per cent. solution of citric acid. In this determination, 200 grams of air-dried soil were treated with 2000 cc. of one per cent. citric acid for forty-eight hours, with occasional shaking. At the end of this time, the solution was filtered, and the iron and manganese determined in the filtrate. The following table will show the results, expressed in percentages of air-dried soil:[2]

TABLE IV.

	Black soil. Per cent.	Red soil. Per cent.
Mn_3O_4	0.733	0.028
Fe_2O_3	0.243	0.379

Estimating that an acre foot of this soil weighs about 3,500,000 pounds, we find that the black soil contains, on an average, about 23,755 pounds of citrate-soluble mangano-manganic oxide per acre foot, while the red soil is found to contain only 980 pounds in the same area. It would, therefore, be extremely surprising if this large amount of soluble manganese were without influence in the soil. It is sufficient here to point out the relations between the citrate-soluble iron and manganese in the soil. From the table, it is shown that these stand in inverse proportions.

In the strong acid digestion of the black soils, it was noticed that considerable frothing or effervescence developed upon slightly heating same,

[1] Cited by Schreiber in *Révue Générale Agronomique*, January, 1906.

[2] *Nineteenth Annual Report of Rhode Island Experiment Station.*

[1] *Bulletin of the College of Agriculture, Tokio Imperial University*, **5**, No. 2, p. 162.

[2] Average of the determination in six samples

and subsequently, this was found to be due to the escape of chlorine gas. Numerous samples have been treated with hydrochloric acid, and in every instance, the black soils have been found to liberate large quantities of chlorine; the red soils do not possess this power.

In the determination of volatile combustible matter, it was also observed that after heating the black soil just below redness for some hours, the sample still retained some of its dark color; but upon subsequent stronger heating, further loss in weight occurred and the soil took on a dark brown color. From these facts, it seems likely that at least a part of the manganese in the black soil exists in the form of higher oxides. The black color and the liberation of chlorine gas suggests the presence of manganese dioxide, or the sesquioxide of manganese.[1] It is, of course, likely that the dark color of these soils is caused, in part at least, by organic matter.

It is reported that in some of these fields, the first crop of pines, on virgin soil, showed but little yellow color during the first twelve months of their growth. Later, however, these plants became very yellow and almost ceased to grow. With the continued growth of pines on this soil, its color also seems to become darker. A number of the yellow plants were pulled up and it was found that the soil adhering to the larger roots was darker in color than the general soil. In this connection, Aso reports that wheat grown in solutions containing a small amount of manganous sulphate was found to contain manganese dioxide adhering to the roots.[2] These facts, together with the observation that the cultivation of pines on this soil renders it less adapted to the crop, indicates that there is some change brought about in the soil by the crop itself; and since the soil of this entire section has arisen from the disintegration of lava, which, in its original state could not have contained either of the black oxides of manganese, it seems reasonable that in the growth of pines, a change in the state of oxidation of the manganese takes place.[3]

In connection with the investigation of the soil, a study of the yellow plants has also been undertaken. It was formerly believed that the etiolated appearance of the pines was caused by some pathological or entomological infestation, but as yet, all efforts to determine such infestation have proven fruitless. No insect or fungus, which is known to produce this phenomenon, has been found on these plants. The root system of the yellow plants was found to be dwarfed and much less extensive than that of vigorous, green plants. In many instances, the roots are covered with a black coat, and have but little indication of life. The yellow plants possess but few root hairs. The healthy, green pines, on the contrary, have a very extensive root system, sometimes reaching out to a distance of several feet from the plant.

[1] See "Soils" by Hilgard, p. 283.

[2] *Bull. of the College of Agric., Tokio Imperial University*, **5**, No. 2, p. 183.

[3] See *Bulletin* **56**, *Bureau of Soils, U. S. Department of Agriculture*.

Some analyses of the ash from both the green and yellow plants have been made, and while a sufficiently large number of plants have not been analyzed to warrant positive conclusions, it seems that the entire metabolism of the yellow plants has been disturbed. A number of young plants, about four months old, taken from both red and black soils, and also an equal number of plants two years old, were examined. A composite sample, made up of an equal number of leaves from the same portion of these plants, was analyzed. In the following table the percentages of manganese oxide in the ash of these plants is given.

TABLE V.

	Yellow pines (4 months old). Per cent	Yellow pines (2 years old). Per cent.	Green pines (4 months old). Per cent.	Green pines (2 years old). Per cent.
Mn_3O_4	2.12	1.15	1.65	1.68

In consideration of the very large percentage of easily soluble manganese in this soil, it is rather surprising that a higher percentage of this element is not found in the pineapples grown thereon, especially, since it is generally considered that in the presence of soluble substances, plants have the power of taking up these substances in considerable quantities.

In this connection, it has been pointed out that many plants contain notable amounts of manganese. Schröder,[1] for instance, found that the ash of the leaves of Norway spruce contained 35.53% Mn_3O_4, while the ash of the bark of this tree was found to contain 41.23% Mn_3O_4. It is interesting here to note the smaller percentage of manganese in the ash of the yellow plants two years old, than is found in younger pines. In the case of green plants, the ash is found to contain about the same percentage of manganese in each of the two stages.

The fact that other plants, such as wheat, barley, etc., grown under normal conditions, con-

[1] Cited from *Jahresbericht der Agrikulturchemie*, **1**, 110 (1878).

tain not only a higher percentage of nitrogen and potash, but also more of these substances in actual pounds, during the advanced growing period than at maturity, has been pointed out by several investigators. In a very exhaustive investigation of this subject, Wilfarth and Römer,[1] at the Ducal Experiment Station, have shown that the decrease of the actual total nitrogen and potash in wheat and barley, as these plants pass from the growing stage into maturity, can be explained in no other way than that these substances are actually returned to the soil. These investigators found that of the potash in wheat and barley, at the time of flowering, only 58.87% of that in the former, and 64.97% in the latter, remained at maturity. Whether potash, for instance, after having performed its function is excreted through the roots of these plants, or from their leaf surfaces, and then washed to the ground by subsequent rains, as has been suggested by some investigators,[2] the results would be the same, namely, a decrease in the potash content of the plant; and while it is true that potash is necessary to plant growth, and manganese is not usually so considered, the suggested analogy in the two cases is none the less interesting.

Manganese, when applied in small quantities, has been shown by several workers to produce the effect of stimulation. Nagaoka,[3] at the Tokio Imperial University, effected an increase in the yield of rice to the extent of 37 per cent. by the application of 77 kilos of manganous sulphate per hectare. At the Woburn Experiment Station, the stimulating power of manganese on wheat and other crops has also been determined, and other investigators have found that small amounts of various manganese compounds produce the same effect. The fact, however, that small quantities of a substance can exert a stimulating effect, does not necessarily imply that larger quantities would be beneficial. In the animal organism, for instance, a small amount of alcohol is known to produce the effect of stimulation, whereas larger amounts have a depressing effect. The same may be said of ether and chloroform. With plants, there are several well-known examples of the same condition. Katayama[4] and others

[1] Researches from the Ducal Agric. Expt. Station on "The Assimilation of the Elements of Nutrition by Plants during Different Periods of Their Growth," *Die landwirtschaftlichen Versuchsstationen*, Vol. 63, 1905.

[2] LeClerc and Breazeale, *Science*, **28**, 216 (1908).

[3] *Bull. College of Agric., Tokio Imperial University*, **6**, No. 1.

[4] *Ibid.*, **7**, No. 1.

have shown that ferrous sulphate in small quantities produces a stimulation of certain plants, and whether or not this is brought about by bringing into solution some of the dormant bases of the soil, larger quantities of this substance are often referred to as actually poisonous to plants.[1] Sutherst[2] has shown that while the application of small amounts of various manganese compounds, including the dioxide, has a stimulating effect on maize, he points to the work of Salamone as indicating that larger amounts of these substances are detrimental.

The question of how these substances produce stimulation, in small quantities, and a depressing effect, when present in large quantities, is not thoroughly understood, but that such is the case is generally accepted. Aso,[3] for instance, has shown that a given amount of manganese may produce stimulation of rice, whereas the same amount of this element, when applied to wheat and barley, may, under certain conditions, result in decreased vigor and the development of a yellow color in the plant. This author has further pointed out that the depressing effect of such applications of manganese is usually more marked in cold weather than in warm, and with the return of warm weather, in some instances, these plants were able to entirely overcome the stunted growth and yellow color.

We find a parallel condition in Hawaii, where the pineapples on soils which contain an intermediate quantity of manganese, have been repeatedly observed to become decidedly yellow during the winter months, but such plants sometimes entirely overcome this condition with the return of warm weather. It should be mentioned in this connection that sugar-cane grows exceedingly well on these manganese soils, where pineapples refuse to grow.

Bertrand,[4] some years ago, found that the ash of oxidizing enzymes contains considerable amounts of manganese, and that the addition of soluble manganese salts to the oxidases greatly accelerated their oxygen-carrying power. Woods[5] has shown that the yellow spots, which sometimes occur on the leaves of certain plants, have a greater oxidizing power than the green parts of the same

[1] "Agriculture" by Storer, Vol. I, p. 216

[2] "Manganese Compounds as Fertilizers for Maize," *The Transvaal Agric. Jour.*, **6**, No. 23.

[3] *Bull. College of Agric., Tokio Imp. University*, **5**, No. 2, pp. 177–185.

[4] *Compt. rend.*, **124**, 1032.

[5] Abstracted in E. S. R., **12**, 216.

plant. In seeking an explanation of the yellow color produced by the application of manganese sulphate to barley, Loew and Sawa found that such plants are more vigorous oxidizing agents than those not treated with manganese. Summarizing their observations, they say: "Manganese exerts, in moderate quantity, an injurious action on the plants, consisting in the bleaching out of the chlorophyl. The juices of such plants show more intense reactions for oxidase and peroxidase than the healthy control of plants. Manganese exerts further a promoting effect on the development, still observable in high dilution, while the injurious effects disappear under this condition. It is probable that soils of great natural fertility contain manganese in an easily absorbable condition, and this forms one of the characteristics of such soils."[1]

With the view of determining whether yellow pineapple plants contain a more active oxidase than green plants, a number of experiments were made. After some preliminary tests, it was found that the tissues of this plant contain some substances, possibly tannins and certain sugars, which hinder the reaction. In many instances, the blue color produced upon the oxidation of guaiacum was found to soon fade out. Certain substances are known to hinder this reaction, and some investigators have taken advantage of the fact that these bodies are soluble in 80 per cent. alcohol, whereas the oxidizing enzyme is precipitated by this reagent. In this determination, the yellow and green leaves were thoroughly crushed, extracted several minutes with 80 per cent. alcohol, then the insoluble portion was taken up with 30 to 40 cc. of distilled water, and allowed to stand an hour. Five cc. of this extract were then tested for oxidase, using the guaiacum and aloin tests, with the following results:[2]

TABLE VI.

	Guaiacum	Aloin.
Yellow leaves.	Deep blue.	Rose-red.
Green leaves	Pale blue.	Faint red.

From the above table, it is shown that the plants grown on the soil containing high percentages of manganese contain a more active oxidase than plants from soil containing little manganese, and whether the increased activity of the oxidase in the yellow plants brings about their etiolated appearance, by the actual oxidation of the chlorophyl or for other reasons, cannot be positively stated at this time. An examination under the high-power microscope of the cross-section of the yellow leaves, shows, however, that for the most part the chlorophyl bodies have been entirely destroyed. Further investigation, it is hoped, will throw more light on this subject.

SUMMARY AND CONCLUSIONS.

1. Some of the pineapple soils of Hawaii contain black spots on which pineapples turn yellow and do not grow successfully.

2. The application of fertilizers and lime, in conjunction with good tillage and drainage, has not resulted in effectually overcoming the yellow appearance of the pines on black soil.

3. The black soils contain less acidity than the red soils.

4. There is but one important difference in the chemical composition of these soils, *viz.*, in regard to the manganese content. The black soils contain many times as much manganese as the red soils. A close correlation was found to exist between the degree of yellowing of the pines and the percentage of manganese in the soil.

5. The black color of these areas may, in part, be attributed to the presence of higher oxides of manganese.

6. Yellow pines from soils containing a high percentage of manganese are more active oxidizing agents than green plants from red soil. Also the yellow pines have a poor root system and contain but little chlorophyl.

This investigation is being continued along the lines suggested in this paper. Acknowledgments are due Miss Alice R. Thompson, assistant chemist, for assistance in this work. A large part of the analytical work was done by her, and many valuable suggestions were offered from time to time. Also to Doctor E. V. Wilcox for the microscopic examination of these plants, and for many very valuable suggestions.

[1] *Bulletin College of Agric., Tokio Imp. University*, **5**, No. 2, p. 172.

[2] See "Peroxidase Accelerators and Their Possible Significance for Biological Oxidations," by Kastle, *American Chemical Journal*, **40**, No. 3.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

METHOD FOR DETERMINING SODIUM BENZOATE IN KETCHUPS OR OTHER FOOD MATERIALS.

By WILLIAM E. HILLYER.

Received May 5, 1909.

The work reported in this paper was done during the year 1908, to establish a satisfactory method

for determining sodium benzoate in food products. Experiments were conducted, applying the present provisional method of the Association of Official Agricultural Chemists to water standards as well as to ketchup containing known amounts of sodium benzoate. Unsatisfactory results were obtained in every case as varying amounts were recovered. The chief sources of error are (1) the impossibility of preventing moisture from getting into the weighing tubes, (2) the loss of benzoic acid in the sublimation process through imperfect joints, and (3) the difficulty of obtaining complete volatilization of the benzoic acid or its complete condensation in the weighed collection tubes.

In order to obviate these difficulties, the following method was developed, based on the difference in the solubility of silver benzoate and that of silver nitrate in ethyl alcohol. One liter of ethyl alcohol dissolves 0.169 gram of silver benzoate while one liter of the same solvent takes up 31 grams of silver nitrate.[1]

The best results in extraction were obtained by diluting the ketchup with as little water as possible so that the total quantity of ether used to extract the benzoic acid is in excess of the water solution and also by having a larger excess of salts present which changes the specific gravity of the liquid and permits a better extraction by the ether.

The author's present practice with the ketchup is as follows: Weigh 100 grams and wash into a 300 cc. graduated flask, make alkaline with ammonium hydroxide, add about 5 grams of powdered salt and 5 cc. of milk of lime, make up to the mark, and filter. Acidify 150 cc. of this filtrate with 1:1 hydrochloric acid and extract with four separate portions of ether, using 100 cc. each time, care being taken to prevent the formation of an emulsion. The quantity of ether is specified at 400 cc. in order to give a large excess of this solvent for the benzoic acid over the dissolving power of the water that is present. A maximum degree of extraction is thus obtained.[2]

Evaporate at room temperature to dryness, or if the ether is distilled, care should be taken that none of the volatile benzoic acid is driven off by using too high a temperature.

Dissolve the residue, using no more absolute alcohol than is positively necessary. Absolute alcohol must be used in the case of ketchups and other material in which the water held by the ether carries down water-soluble substances insoluble in alcohol; by using water-free alcohol, they are eliminated at this point. Just neutralize this alcoholic solution of the benzoic acid with an alcoholic solution of sodium hydrate, using a drop or two of phenolphthalein as an indicator.

Evaporate to dryness at a gentle heat. Direct evaporation on the steam bath is liable to carry off some sodium benzoate owing to the attraction of the alcohol up the sides of the beaker, so gently heat by interposing an iron plate and sheet of one-quarter inch asbestos between the steam bath and the beaker.

The solution containing sodium benzoate could at this point be evaporated to about 10 cc. in volume instead of to dryness and then precipitated with silver nitrate solution; but, especially in the case of ketchups, it was found that by adopting the latter course, substances insoluble in alcohol appear and may be filtered off and eliminated.

Redissolve the residue from this evaporation in alcohol saturated with silver benzoate made up as follows: allow pure aldehyde-free alcohol (prepared as described in *Bulletin* **107,** *Rev.*, *Bureau of Chemistry*, page 96) to stand over silver benzoate until saturated. This alcohol, when filtered, is the reagent used throughout the method when an alcohol solution is specified.

Filter off any residue not soluble in the alcohol and precipitate as silver benzoate by adding 10 or 15 cc. of the silver nitrate reagent (prepared by dissolving to saturation, pure, pulverized, silver nitrate in the alcohol solution, and filtering).

Filter at once on a small asbestos Gooch prepared to filter quickly with moderate suction. Wash first with a few cubic centimeters of the alcohol solution and finally with a few cubic centimeters of ether. Dry in the water oven for a short time, until the ether is driven off; cool and weigh.

It was experimentally established in developing the method, that water solutions of sodium hydrate for neutralizing, or of silver nitrate for precipitating would not yield acceptable results because of the solubility of silver benzoate in water. One liter of aqueous solution contains 1.763 grams of silver benzoate at 14.5° C. and 2.607 grams at 25°.[1]

The following table will show the results obtained in developing this method.

[1] Taken from Seidell's "Solubilities of Inorganic and Organic Compounds," pp. 279 and 289.

[2] The author has been informed that the report of the referee on preservatives of the Official Association of Agricultural Chemists for 1908 states that chloroform is a better medium for extracting benzoic acid, as less foreign substances are removed.

[1] Hollman's *Physik*, **2**, 129 (1893). Through Seidell's "Solubilities of Inorganic and Organic Compounds," page 279.

Table 1. Extraction of Benzoic Acid with Ether from a Water Solution.

Sample number.	Amount used. Gram	Amount extracted. Gram
1	0.1	0.091
2	0.1	0.1018
3	0.1	0.102
4	0.1	0.114
Average		0.102

This table shows that the process of extraction with ether is complete. The result on sample No. 4 is probably due to incomplete drying.

Table 2. Experiments on the Use of Weighed Filter Papers for Final Weighing.

(Water solution of sodium benzoate + 1 H_2O used.)

Sample number.	Amount of sodium benzoate present. Gram.	Weight of silver benzoate obtained. Gram	Sodium benzoate recovered. Weight.[1] Gram.	Sodium benzoate recovered. Percentage.
1	0.100	0.1366	0.1122	112.0
2	0.060	0.077	0.0545	90.8
3	0.060	0.0786	0.0556	92.70
4	0.030	0.0300	0.0212	70.0
5	0.030	0.0326	0.0231	77.0

The use of a tared filter paper for final weighing does not give as satisfactory results as when an asbestos gooch is used.

Table 3. Application of the Final Method to Water Standards.

(Using a water solution of sodium benzoate − 1H_2O and an asbestos gooch.)

Sample number.	Amount of sodium benzoate present. Gram.	Weight of silver benzoate obtained. Gram.	Sodium benzoate recovered. Weight.[1] Gram.	Sodium benzoate recovered. Percentage.
1	0.030	0.043	0.0307	102.0
2	0.030	0.041	0.029	96.7
3	0.030	0.040	0.0283	94.4

Table 4. Application of Method to Ketchups Containing Known Amounts of Sodium Benzoate.

(Gooch asbestos filter used.)

Sample number	Sodium benzoate added Gram.	Weight of silver benzoate obtained Gram	Sodium benzoate recovered. Weight [1] Gram	Sodium benzoate recovered. Percentage.
1	None	0.0000	0.0000	.....
2	"	0.006	0.004	.....
3	"	0.0009	0.0006	.....
4	"	0.0000	0.0000	.....
5	"	0.004	0.0028	.....
6	"	0.004	0.0027	.....
7	"	0.0019	0.0014	.....
8	0.030	0.041	0.0290	97.0
9	0.060	0.090	0.0637	106.0
10	0.060	0.0783	0.056	93.0
11	0.060	0.0783	0.056	93.0
12	0.060	0.0792	0.0560	93.5
13	0.060	0.0834	0.0591	98.5
14	0.100	0.1410	0.1005	100.5
15	0.100	0.1410	0.0996	99.96

This method has been used in the routine work of analyzing commercial samples of wine, jams, ciders, molasses, sirups and ketchups, in the Division of Foods. The method has also been submitted to other laboratories for collaborative work and for comparison with other proposed methods. Tabulated results of this work are given in *U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin* **122**, *Proceedings of the Association of Official Agricultural Chemists for 1908*.

[1] Calculated from preceding columns.

ECONOMIC REASONS FOR THE REDUCTION OF MILK TO POWDER.[1]

By Lewis C. Merrell.

Received May 3, 1909

The present method of milk supply is wasteful, uneconomical and generally unsanitary. It is not to be supposed that a civilized community in which sanitary science is advancing so rapidly will continue to tolerate the menace of impure milk, when a satisfactory solution of the whole milk question is offered.

While the production of certified milk offers decided advantages over old methods in the matter of cleanliness, it by no means solves the universal milk question, for there is no present prospect of a sufficient supply of certified milk to make its use at all common, and the expense of producing it places it beyond the reach of the modest income except for the special uses of infant and invalid.

Contrary to general opinion, the production of clean milk is not much more expensive than the production of unsanitary milk. The expense necessary in the production of certified milk is chargeable rather to methods and apparatus used in keeping the milk clean from contamination and protecting it from unfavorable conditions during shipment and storage. Such experience as I have had in the production of clean milk leads me to believe that any careful farmer with a reasonably well equipped dairy can produce milk containing not more than twenty-five hundred to four thousand bacteria per cc. in the milk pail. The bacteria count of this same milk at subsequent stages depends entirely upon the conditions under which the milk is kept. My point is that good, clean milk, well below the certified milk limit as to bacteria count, can be produced without much additional expense in any dairy, but the expense involved in preparing such milk for the market, that is to say the expense of preserving it, is such as to make the use of certified milk very limited.

It is apparent that we need an inexpensive method of preserving milk for the market, a method

[1] Read before the Syracuse Section of the American Chemical Society, November 23, 1908.

less expensive than is employed in preparing certified milk so that it will keep.

The ideal method of milk preservation should prevent decomposition or increase of bacteria count, without the use of preservative substances, without changing the chemical composition of the material or be preserved, and without altering such characteristic qualities as taste, odor and appearance.

All these advantages may be secured, as I will presently show you, by a properly conducted system of desiccation. This will at the same time prevent injury to the milk from extremes of heat and cold and will eliminate the possibility of contamination during shipment and storage. Reduction of bulk and weight are also secured, resulting in considerable saving in freight.

Before entering into a further discussion of the advantages and possibilities of milk desiccation, I wish to take up, in a general way, the composition of milk and explain some of the difficulties which have tended to prevent the accomplishment of this extremely desirable result, namely, the reduction of the solids of milk to a powder.

I will take the following analysis as typical of an average milk:

Fat	3.60
Milk sugar	4.58
Casein	2.81
Albumen	0.56
Ash	0.75
Solids	12.30
Water	87.70

If we remove the moisture from this milk, we will have approximately the following analysis:

Fat	29.27
Milk sugar	37.24
Casein	22.85
Albumen	4.55
Ash	6.09

Let us consider these different constituents in their relation to desiccation.

If the butter-fat of milk is heated for a considerable length of time, especially if in contact with a heated metal surface, the butter-fat loses its finely subdivided globular condition and melts into a grease. For this reason all milk-desiccating processes, which require heating the milk in a container or upon a metal surface, have been most successful with milk from which the cream has been separated. If any desiccated milk is to solve the problem of our milk supply, it must contain all the cream, in no wise altered from its natural condition.

Milk sugar presents few obstacles in the desiccation of milk, provided the temperature be kept below 212° F. This temperature may be exceeded for short periods of time without caramelizing the milk sugar, but great care must be exercised. Some processes depend upon desiccation *in vacuo* to prevent the browning of the milk sugar. That this is not always successful is due to the fact that in order to maintain sufficient temperature within the vacuum to cause boiling and consequent evaporation of the water of the milk, it is necessary to use a temperature above 212° F. in the steam jacket of the vacuum chamber. Hot water has been tried as a source of heat but it renders the evaporation so slow as to be impracticable. The wall of the vacuum chamber, therefore, is above 212° F. even though the interior atmosphere of the chamber is only 130° to 140° F. In consequence of the temperature of the chamber wall, some of the milk sugar is usually discolored.

Lactic acid, while not mentioned in the above analysis, is always a constituent of milk. It results from bacterial action upon the milk sugar, and exists in larger or smaller amounts according to the care with which the milk has been drawn and kept. It is not decomposed by any drying process, but will, under certain conditions, combine with other constituents of the milk, giving undesirable results. The removal of the water from milk concentrates the acid to eight times its strength in the liquid milk. A good quality of fresh milk will contain from ten to fifteen hundredths of one per cent. acid. When this same milk is reduced to dryness, its solids will contain approximately one per cent. of acid.

One of the constituents of milk which is affected by this concentration of the lactic acid is casein, which is precipitated from its normal suspension and becomes insoluble. This effect is more pronounced under the influence of heat. It is sometimes avoided by neutralizing the acidity of the milk with suitable alkalies. If this is overdone, a soapy taste is imparted to the milk, and even if the neutralizing is accurately performed, the milk tastes salty on account of the formation of lactates. If desiccation is performed at a comparatively low temperature and very rapidly, the concentration of the acid has very little effect on the casein.

The other constituent of milk which is affected by the concentration of the lactic acid is the albumen. Unlike the casein, the lact-albumen is in true solution. It is coagulated by acidity and heat,

and even though the acidity be neutralized, the coagulating effect of the heat cannot be avoided as with casein. This coagulating effect is produced at any temperature above 149° F. and depends upon the length of time of the exposure to heat. It is evident that to avoid coagulating the albumen, either a very low temperature must be employed in desiccation or else that the drying must be accomplished in a space of time decreasing in length as the temperature increases. No process of desiccation which depends upon reduction to dryness by boiling in open air or *in vacuo* has ever, so far as I am aware, produced a milk powder containing a completely soluble albumen.

The relation of the milk salts to desiccation is not important and I will not discuss it here.

There is still a further difficulty which lies in the way of those who have attempted to reduce milk to dryness. When its water content is reduced below 40 per cent., it acquires a consistency somewhat like library paste. After it reaches this condition, it is very hard to dry. It does not reach a condition where it can be powdered until the water content has been reduced to perhaps 10 per cent. It differs in this respect from most other food substances that are ordinarily dried. I had occasion some time ago to make some exper ments with starch. The particular sample I was examining became liquid with a water content of 55 per cent. When this water content was reduced to 50 per cent. by the addition of more starch, the starch became solid and capable of being powdered. There was no intermediate sticky, pasty condition. It is this peculiarity of milk more than anything else that prevented the perfection of a satisfactory milk-desiccating process for more than fifty years. When milk is in this condition, it is very easily injured by heat. The water cannot be boiled off for bubbles cannot rise through the sticky mass. In fact, the water is very difficult to remove in any manner.

Various methods have been employed for treating milk to remove the moisture while in this sticky state, as for instance stirring *in vacuo*, pressing through a shredding machine, and exposing to dry air, rolling into thin sheets either *in vacuo* or in the open air upon a heated surface and scraping the dry material off with a knife. All of these methods require so much mechanical manipulation, rubbing and stirring of the pasty milk, that the globular form of the butter-fat is destroyed, and the manufacturers are unable to make a whole milk powder or a cream powder that resembles fresh milk and cream when dissolved, nor are they able to manufacture a powder containing butter-fat that will keep. There is no reason why the butter-fat of milk should not keep if its original globular form is preserved. Many seeds and different kinds of meal and flour contain large percentages of fat and oils, which do not become rancid unless the substance be heated or otherwise treated so as to break down the globular structure of the fat or oil, when it becomes rancid. A good illustration of this is the peanut. It contains a large amount of oil, yet does not become rancid while raw. After it is roasted the oil soon begins to oxidize, and the peanut butter, which is the expressed oil of the peanut, becomes rancid very easily.

I said earlier in my paper that a properly conducted system of milk desiccation was the ideal method of milk preservation, preventing decomposition or increase of bacteria count, without the use of preservative substances, without changing the chemical decomposition of the milk and without altering its state, odor and appearance. I will now describe such a process, showing you how the difficulties before mentioned may be avoided and a perfect milk powder be produced which offers all the advantages of certified milk at a much less cost.

Fresh whole milk is drawn into a vacuum pan and a portion of its water removed. This condensation is halted while the milk is still in a fluid condition and before any of the milk albumen has been cooked on to the walls of the vacuum chamber. The milk is then drawn from the vacuum pan and sprayed into a current of hot air. The moisture of the milk is instantly absorbed by the air and the particles of milk solids fall like snow. Upon examination, they are found to contain less than 2 per cent. and sometimes not more than one-half of one per cent. of moisture. The hotter the air is the more rapid the drying effect and the less danger there is of injuring the milk solids by heat. I say this advisedly. Let us assume that each little particle of milk is a sphere, and that evaporation is proceeding upon all portions of its surface. This evaporation not only takes heat from the air, but also from the interior of the milk particle, so that the milk solids become cooler and cooler until completely dry. After that, the temperature does not affect them.

As illustrating the fact that thoroughly dried albumen cannot be coagulated by heat, I took

a sample of egg albumen, dried by this process, and hermetically sealed it in several cans. These cans were placed in boiling hot water for periods varying from one-half to four hours. Afterward the albumen was examined for solubility which was found not to have been impaired, the albumen in the can subjected to heat the longest showing the same solubility as the original unheated albumen.

This method of desiccation does not destroy the globular condition of the butter-fat, it does not burn the milk sugar nor does it coagulate the albumen of the milk. It is not necessary to neutralize the acidity of the milk, for the moisture is removed so quickly that there is no chance for chemical action, and neither the casein nor the albumen are affected in any way by the concentration of the acid. The difficult pasty condition of the milk solids is passed while the milk particle is suspended in the air and not in contact with heated metal. As nearly as I can estimate, one pint of milk presents about two acres of surface when sprayed into the air. The individual dried particles are from one two-thousandth to one ten-thousandth of an inch in diameter.

No bacterial action has been discovered in milk powder containing less than 3 per cent. moisture, and no chemical deterioration takes place. It is, therefore, evident that the milk powder product described above, fulfils my definition of an ideal preserved milk, for decomposition is prevented merely by dryness and without the use of preservative substances and without changing the chemical composition of the milk. As to the odor, taste and appearance, I will leave you to judge from the samples I will show you. I will say, however, that this whole milk powder is in use in place of fresh milk at several of the United States soldiers' homes and military posts as well as in the navy. It has been subjected to the most exhaustive tests by the United States Department of Agriculture, Bureau of Chemistry, and by the Experiment Stations of different states. The Pacific fleet carried a ton of it around the Horn under an absolute guaranty as to keeping quality and has since reordered largely. A 10c package makes one and a half quarts of milk, at \$0.06 2/3 a quart. With these results in mind it is not too much to assume that the reduction of milk to powder offers a satisfactory solution of the universal milk question.

Primarily there are two reasons for the preservation of any perishable food substance: in the first place, that it may be stored for future use and in the second place so that it may be transported from place to place economically while retaining its desirable qualities. Both of these reasons apply with special force to milk which is one of the most difficult of food substances to store and transport.

Giving our consideration to the first of these questions, there are several important reasons for the preservation of milk by reducing it to powder. Two-thirds of the milk supply is produced in six months from April to September, and the remaining one-third in the six coldest months of the year. The price drops in summer because the supply exceeds the demand and because milk is more difficult to keep in the hot weather. The price rises in winter because the demand exceeds the supply. The surplus in summer goes into butter and cheese but there is no way to augment the winter supply when it falls short. The storage of whole milk in summer in the form of a powder assures the country of an adequate supply in winter. The storage of food always tends to steady prices, enabling merchants to do business on smaller margins, thus reducing prices to the community in general. The advantages of storing fresh milk for future use on the sea and in very cold and very hot climates are well understood and need no comment here.

The second reason for the preservation of milk, namely, that it may be transported from place to place economically without deterioration is probably even more important. There is great difficulty and expense connected with the transportation of a highly fluid and perishable substance like milk. New York City gathers its supply largely within a radius of three hundred miles though in certain cases milk for domestic consumption is drawn four hundred miles to New York. The daily average of milk required to supply New York City during 1907 was 49,306 cans, an increase of 1335 cans per day over 1906. The freight rate was \$0.23 for the first forty miles, \$0.26 for the first one hundred miles, \$0.29 for the first one hundred and ninety miles and \$0.32 for all beyond this distance. If a person were to ship milk from the outer zone to New York City, it would cost \$0.32 for a forty-quart can containing eighty-five pounds of milk. A discount of 15 per cent. is allowed on carload lots of not less than 10,000 quarts, making a net cost per can \$0.272. Eighty-five pounds of milk would contain 10 3/4 pounds of powder. Assuming, therefore, that the solids represent the

value of the milk, it would cost \$2.53 to ship to New York, liquid milk equivalent to 100 pounds of powder. The freight rate from the same zone to New York on milk powder is \$0.25 per hundred, in less than carload lots or \$0.18 per hundred in carload lots. As the material is not perishable, it is fair to take the carload rate. We can, therefore, ship for \$0.18 in powder form an amount of milk which it would cost us \$2.53 to ship in liquid form. Besides this, the shipper of liquid milk runs the risk of having his milk spoil, while the shipper of milk powder runs no such risk. The cost of shipping the milk in powder form is only about 7 per cent. of the cost of shipping the same amount of milk in liquid form. Assuming that the average rate per can to New York is \$0.25, it cost last year \$12,326.00 per day freight on New York supply of milk. This same milk could have been delivered in New York in the form of powder for \$863.00 per day, a saving of \$11,463.00 per day, a saving of \$4,183,995.00 per year.

The average cost of New York's supply of milk is \$1.30 per forty-quart can or \$0.03¼ per quart, delivered at New York. This milk costs the New Yorker about \$0.08 a quart, leaving a margin of \$0.04¾ per quart for cost of delivery and profit to the dealer. The same amount of milk can be delivered to the consumer in the form of powder on a margin of \$0.02¼ per quart for cost of delivery and profit to the dealer, showing a saving of \$0.02½ per quart over present methods. This would mean a saving of \$0.90 a can or \$44,375.00 per day on New York's milk supply, a saving of \$16,197,021.00 per year over present methods. I am assuming that the grocer handles this milk powder on regular margins, namely 20 per cent. for the retailer and 10 per cent. for the wholesaler.

At \$0.08 per quart New York's milk supply is worth \$57,589,408.00 per year. I have shown above a saving per year of \$16,197,021.00 on dealers' profit and cost of selling, amounting to about 28 per cent. of what New York City's inhabitants pay for milk. On this basis milk could be sold in New York City in powder form at an equivalent of \$0.06 per quart and afford an attractive margin of profit for all concerned, the saving in freight being sufficient to pay the cost of reducing the milk to powder, and the manufacturer's profit.

There are no reliable data available as to the consumption of fresh milk per capita, but the constant rate of increase in the number of cows in proportion to population may be taken as indicating a continual increase in the consumption of fresh milk. Milk is not, however, by any means as widely used as it should be. This is partly due to the reluctance of the housewife to purchase an ample supply, owing to its perishable nature. It is a well-known fact that convenience increases use. Street cars are more depended upon when they run every three minutes than if there are five-minute intervals, for many people who would walk rather than wait, will ride if there is a car at hand. The average housekeeper takes a given number of pints or quarts of milk a day. Some days she needs more than she has, other days she has more than she needs. Either she is wasting money by buying too much or else the milk dealer is losing business. It is evident that with a powdered milk always on hand ready when wanted, the use of milk would be popularized.

In England where ice is but little used for preserving food, the housewife buys only as much of meat or vegetables as can be used during one day. Milk peddlers are passing in London every few minutes and milk is bought only when wanted. Such methods seem strange to us because we are accustomed to depend upon preservation of food by ice. It is not impossible therefore that our present method of supplying milk may seem strange to people a few years from now, when milk powder has become a staple article like flour.

One reason for the expensiveness of a house-to-house delivery of liquid milk is the fact that the demand for milk varies considerably from day to day, whereas the cow pays no attention to the whims of the public. The milk dealer must always have enough to supply his patrons when the demand is large. At other times he must make butter and Dutch cheese out of his surplus milk and lose money on every quart of milk utilized in this way. I am told by a prominent milk dealer that the demand for milk is usually large on Monday. On Tuesday it is very small. On Wednesday it recovers and on Thursday it drops away again. On Friday it is large and on Saturday his demand always exceeds his supply. A permanent product would adjust supply to demand every day in the week.

Another economic reason for the reduction of milk to powder is the fact that there are many districts which are eminently suited to milk production where the dairy industry does not thrive because of their distance from market. The

location of milk-desiccating plants in such districts would do much not only to promote the interests of remote farming communities, but would largely increase the milk supply of the country. The question of time would be entirely eliminated and the distance from market would not be a factor except for a slight increase in freight rate. It is well known that the railroads make very close rates on long distance shipments of western products to eastern states and in fact the freight rates from Illinois and Iowa may be lower to New York than from some district in northern Vermont or northern New York. There is no reason therefore why New York City should not draw its milk supply from the western states as it now largely draws its supply of butter and eggs.

In fact most of the economic reasons for the reduction of milk to powder might be summed up in one phrase, a world market for milk.

There is one reason, however, which I wish to dwell upon that is rather sanitary than economic. Fresh milk is a substance upon which no pure food guaranty is possible. It is drawn to-day and gone to-morrow. This renders adequate milk inspection practically impossible. With milk supplied in the form of a permanent powder, it is entirely possible to create a high standard of quality and purity because the stability of the product would permit of the enforcement of rigid regulations.

ON SOLUBLE, FUSIBLE, RESINOUS CONDENSATION PRODUCTS OF PHENOLS AND FORMALDEHYDE.[1]

By L. H. Baekeland, Sc.D.

Received May 15, 1909

In a former paper[2] I have described the conditions under which the condensation of phenols and formaldehyde may produce infusible, insoluble, homogeneous bodies of great chemical inertness which can be used for many technical purposes.

I stated then and there that, starting from the same raw materials, but operating under slightly modified conditions, we may obtain, in other instances, resinous substances which are soluble and fusible and of very different chemical properties.

As far as I know, Blumer[3] was the first one to publish an attempt to utilize this reaction commercially for the manufacture of a shellac substitute. He boiled two molecules of formaldehyde in solution with two molecules of a phenol and one molecule of an oxyacid (tartaric acid) and thus prepared a resinous mass which is purified by washing and can be melted like any ordinary resin and is soluble in alcohol as well as in watery solutions of NaOH. This substance, according to its method of preparation and the amount of free phenol it contains, may be made to melt at widely variable temperatures ranging from 50° C. to considerably above 100° C. According to whether it is prepared with pure white phenol or dark commercial cresol, it will vary in hardness or color. It is always more brittle than shellac and its appearance may vary from that of a colorless transparent vitreous mass to yellow, brown or black. It dissolves in alcohol in all proportions and gives a varnish which dries in about the same way as an alcoholic solution of shellac, but the layer it leaves after thorough evaporation is not so elastic nor flexible as that of shellac and is more brittle; this is probably the reason why it does not sand-paper nor polish as well as shellac. Furthermore, this varnish has a decided tendency to oxidation. The alcoholic solution, which can be made colorless, assumes a darker color after a few days and may keep on darkening until it finally becomes deep ruby. In the same way, objects varnished with this solution will ultimately acquire a decidedly darker color which in time becomes a deep red mahogany stain.

This resin does not dissolve well in weak alkalies like shellac does, but it is soluble in aqueous NaOH. The latter solution oxidizes rapidly in the air and may acquire a vivid purplish red color. Carbonic gas and any acids reprecipitate the resin from this alkaline solution.

The varnish made with the resin obtained from commercial impure phenol or cresol has a decided coal tar odor, which clings persistently to all objects coated with it.

This resinous material is decidedly different in chemical and physical properties from the product described by me as Solid A, or Initial Condensation Product,[1] from which it is easily distinguished by its great tendency to oxidation and its inability of being transformed by simple heating under pressure into Bakelite C. At the time when Blumer published his English patent, he seems to have given considerable importance to the chemical rôle the oxyacid plays in this reaction. However,

[1] Read before the New York Section, May 14, 1909.

[2] "The Synthesis, Constitution and Uses of Bakelite." This Journal, **1**, 149.

[3] Louis Blumer, Eng. Pat., June 5, 1902, No. 12,880.

[1] *Loc. cit.*

later on, both Blumer and DeLaire[1] published processes where the same resin was obtained by the use of mineral acids as condensing agents.

In both methods as published, relatively large amounts of formaldehyde are used, namely about equal molecular proportions.

Furthermore, the amount of acid condensing agent is relatively large and the latter has to be used in rather diluted form, otherwise the reaction becomes violent and irregular. On the other hand, in such diluted mixtures, the reaction begins by separating first a sticky mass containing an excess of phenol while a considerable proportion of CH_2O remains in the supernatant liquid.

To Nathaniel Thurlow belongs the credit of having shown as far back as 1906 that such large amounts of formaldehyde are unnecessary and that they become harmful and produce insoluble bodies similar to the resinous mass described in 1891 by Kleeberg,[2] every time the reaction is conducted so that not too much formaldehyde escapes or remains uncombined. Thurlow used relatively small amounts of hydrochloric acid and kept the reaction under steady control by conducting it gradually and avoiding too violent self-heating during the first stages of the process. He thus succeeded in preparing more economically, a soluble fusible resin entirely similar to those described by Blumer and by DeLaire.

DeLaire, in his French patent,[3] mentions how this same resin can be obtained industrially by first making an alkaline solution of a phenol-alcohol, and uses practically the same process as the one published many years ago by Lederer and by Manasse,[4] which consists in dissolving one mole. of a phenol in one mole. of NaOH, which gives a phenolate, then adding one mole. of CH_2O and after the reaction is over introducing enough HCl to liberate the phenol-alcohol. The latter, in presence of an excess of HCl and more especially under the action of heat, gives resinous matters called saliretins known long ago.[5]

On the other hand, I have shown that if a pure phenol-alcohol, for instance saligenin, be heated in sealed tubes at 180° C., we do not obtain a

[1] DeLaire. Fr Pat 361 539. June 8 1905

[2] *Annalen*, **263**, 283 (1891).

[3] DeLaire, French Pat. 361,539, June 8, 1905.

[4] *Journal praktische Chemie* [2], **50**, 224 *Berichte*, **1894**, 2409-2411; D. R. P., Bayer, 85,588; U. S. P., Manasse, 526,786, 1894.

[5] Beilstein, "Organ Chemie," Vol. 2, 1896, page 1109; R Piria, *Ann Chem.*, **48**, 75, **56**, 37, **81**, 245; **96**, 357 Moitessier, *Jahresbericht*, 1886, page 676. K. Kraut, *Ann. Chem.*, **156**, 123. Gerhardt, *Ann. Chem Phys.* [3], 7, page 215. F. Beilstein and F Seelheim, *Ann. Chem.*, **117**, page 83

fusible soluble resin as prepared by Blumer, DeLaire and Thurlow, but a saliretin product that is only partially soluble and is no longer fusible although it softens decidedly if heated; this substance is not my so-called Intermediate Condensation Product B, because it cannot be transformed into Bakelite C by plain heating under pressure.[1] I shall mention now that I have succeeded in preparing this fusible, soluble resin by heating a phenol-alcohol in presence of a sufficient amount of phenol.

For instance by heating in sealed tubes at 180° C. for 8 hours, a mixture of 14 mole. of saligenin with at least one mole. of phenol, I obtained a resinous substance which can be melted to a transparent mass, soluble in alcohol in all proportions, soluble in NaOH, and which has all the characteristics of the fusible, soluble, resinous condensation products as described above.

Whenever I used less phenol than the proportion 1 : 14 mole., I no longer obtained a fusible product, but a resinous mass which does not melt but only softens when heated; alcohol and acetone only swell it without dissolving it and its properties are entirely similar to the higher dehydrated saliretins.[2]

On the other hand, if the amount of phenol be increased we obtain a much softer resinous mass, more fusible and better soluble.

We also succeeded in preparing these same varieties by simply heating, in a sealed tube, mixtures of phenol with formaldehyde in presence of a few drops of hydrochloric acid, provided always the amount of phenol was present in sufficient excess over equimolecular proportions, this excess answering to a proportion of 15 mole. C_6H_5OH + 14 mole. CH_2O, or still better with somewhat of an excess of phenol.

Instead of taking an acid as a condensing agent, an acid salt will answer the purpose and even an ammonium salt of the strong mineral acids can be used.[1] If, instead of heating in a sealed tube, the reaction is carried out in an open vessel or even with a return condenser which does not exclude the possibility that considerable amounts of CH_2O may be entrained during the violence of the first stage of the reaction, this may result in a decided alteration of the composition of the mixture so

[1] L. H. Baekeland, *Loc cit.*

[2] Dr. A. H. Gotthelf in repeating this experiment with another sample of saligenin, which was not so pure as mine, had to increase slightly the proportion of phenol before he succeeded in obtaining the fusible resin. His proportions were 13 mole to 1.

that an excess of phenol may become predominant.

Or again the reaction may not be carried far enough so that a large amount of formaldehyde remains uncombined as is the case when organic acids are used as condensing agents.

This explains why under the conditions, soluble, fusible resins may be formed even when the original mixture was made up with an apparent excess of formaldehyde; this explains also why Blumer as well as DeLaire, even when mixing molecular proportions of formaldehyde and phenol, got as a final result a fusible and soluble product. It is self-evident that such methods of preparation involve a decided loss of formaldehyde.

These losses are less liable to occur if the reaction be carried out in sealed tubes.

On the other hand, it is a noteworthy fact demonstrated by my prior work[1] that whenever basic condensation agents are used in small amounts, infusible, insoluble, products are obtained *even if the phenol be used in decided excess* and whether the reaction be carried out in closed or in open vessels.

In other words the formation of fusible, soluble resins or infusible, insoluble condensation products is not merely a matter of proportions as to the amount of phenol, but has more intricate chemical causes.

In either case, if an excess of phenol be used in the original mixture, it will be found to exist as *free phenol* in the final product and can be eliminated as such in several ways.

For instance the excess of phenol can be eliminated by blowing steam through the resin while it is kept in molten condition or by heating the molten mass *in vacuo* until it has reached constant weight. In some instances, I have thus kept this resin fused *in vacuo* for several days in succession at 200° C. until all free phenol was eliminated. Although the hardness of the mass, as well as its melting point, increased somewhat, it did not change into the infusible, insoluble resin.

The same thing happened if the resin obtained by heating together saligenin and phenol was heated *in vacuo*. In both instances a point was reached where no further elimination of phenol takes place.

The remaining mass in both cases has the same composition.

Purification by fractional precipitation of the alkaline solution by means of hydrochloric acid gave the same product.

[1] Baekeland, *Loc. cit*

From the analytical composition of same we may assume an empirical formula, $C_{104}H_{92}O_{16}$, in which case the synthesis by means of oxybenzyl-alcohol and phenol could be expressed as follows:

$$14C_7H_8O_2 + C_6H_5OH = 13H_2O + C_{104}H_{92}O_{16},$$

and the direct synthesis by means of phenol and formaldehyde as follows:

$$15C_6H_5OH + 14CH_2O = 13H_2O + C_{104}H_{92}O_{16}.$$

The analytical results are condensed as follows:

Calculated for $C_{104}H_{92}O_{16}$.	Found: Phenol + CH_2O.		Saligenin + phenol.		After fractional reprecipitation from NaOH solution.	
C = 78.16	78.04	77.95	78.16	78.24	78.24	78.65
H = 5.81	5.79	5.97	5.65	5.75	5.75	5.49
O = 16.03	16.17	16.08	16.19	16.01	16.01	15.86

An attempt was made to establish the molecular weight by the freezing point method. The substance was freed as completely as possible from phenol or other volatile impurities by heating *in vacuo* at the temperature of boiling naphthalene. At first glacial acetic acid, then phenol were used as solvents with the following results.

	Solvent.	Concentration.	Molecular weight
(1)	Acetic acid	1 gm in 23.2	1142
(2)	" "	" " " 12.6	1216
(3)	" "	" " " 34.2	463
(4)	" "	" " " 18.2	943
(5)	" "	" " " 13.3	751
(6)	Phenol	" " " 21.5	809

Result 3 may be unreliable for the reason that in order to have complete solution, it was necessary to let the mixture stand over night thus giving the acetic acid, which may not be an indifferent solvent, longer opportunity to react and disturb the results. In the other determinations, solution was complete in a few hours. In every case, however, some traces of transparent, insoluble matter could be seen suspended.

Admitting an empirical formula, $C_{26}H_{23}O_4$, which would be one-quarter of the formula proposed above, we find that 3 is near its value 399, while 5 and 6 are near twice its value; 1 and 2 are nearly three times this value 1197; and 4 is between twice and three times.

In order to simplify matters, I propose to call this substance *Novolak*.

Salts.—An attempt was made to prepare some metallic salts of Novolak, by first bringing its alkaline solution as near as possible towards neutrality by careful addition of HCl, until the point was reached where permanent precipitation begins, then after filtering, adding solutions of Ca, Ba, Cu, Pb, etc.

Potassium and Sodium Salts.—A solution of these can be made by dissolving the pulverized Novolak in NaOH or KOH solution. Addition of acids

reprecipitates the original resin. Even very weak acids, for instance CO_2, will do this.

Calcium Salt.—Prepared by the potassium salt with $CaCl_2$ solution. Analysis of two different samples gave 3.83 and 3.91 per cent. Ca. Dissolved in alcohol; after re-evaporation dried to constant weight contains 2.79 per cent. Ca.

Fractional precipitation of potassium salt with $CaCl_2$ was tried. After drying to constant weight the first fraction gave 2.48 per cent. Ca and the second 3.52 per cent. Ca.

Combustion gave.	Calculated for $(C_{104}H_{89}O_{16})_2Ca_36H_2O$.
C = 72.70	C = 73.07
H = 5.28	H = 5.60
Ca = 3.53	Ca = 3.52
O = 18.49	O = 17.81

Barium Salt.—Prepared like calcium salt. Analysis gave:

C =	67.36
H =	4.95
Ba =	11.08
O =	16.61

which agrees rather closely with results obtained for the calcium salt if allowance be made for the different atomic weights of Ba and Ca.

Alcohol dissolves the greater part of this salt but seems to decompose it and the soluble portion, after recovery, contains only 6.38 per cent. while a similar treatment with acetone gives a substance containing 3.04 per cent. It may be worth while noting that these amounts represent about one-half and one-quarter of that of the salt washed with water.

Lead Salt.—Obtained by precipitation, contains 28.09 per cent. Pb.

Copper Salt.—Contains 6.42 per cent. Cu.

Aluminum Salt contains 2.87 per cent. Al.

Alcohol almost completely decomposes this salt; the insoluble part on ignition carbonizes slightly but is practically entirely inorganic, while the soluble portion after evaporation and drying contains only 0.03 per cent. Al.

Solubility of Novolak salts:

The alkaline salts are soluble in water. The calcium, barium, lead, copper and aluminum salts are insoluble in water. The calcium and barium salts are almost completely soluble in alcohol; the aluminum salt is almost completely decomposed by alcohol; the lead salt is partially soluble in alcohol, but it has not been determined whether it is decomposed by this treatment; the copper salt acts differently from the others in that the particles swell and become translucent while dissolving partially.

Acetone acts similarly to alcohol. All these solutions, on evaporation, leave a structureless varnish film that darkens rapidly by oxidation in the air.

All these salts are insoluble in benzene, toluene, gasolene and chloroform.

Acetyl Compounds.—Novolak, when boiled with acetic anhydride, gives, after subsequent treatment with water, a white powder, insoluble in alcohol but soluble in acetone. Attempts to obtain it in crystalline form were unsuccessful. Boiling with dilute alkali does not apparently affect it, but concentrated alkali decomposes it.

In whatever way Novolak be prepared, its properties are very distinct from those of Bakelite[1] and it can not be transformed into the latter by simply heating. But I have found that by heating Novolak in sealed tubes at 180° C. under pressure with an excess of formaldehyde solution or any of the polymers of formaldehyde or other compounds which can generate formaldehyde, an infusible, insoluble mass is obtained that does no longer soften under the action of heat, as is the case for saliretin products, but which has all the characteristics of Bakelite C.

On the other hand, I have never succeeded in transforming Bakelite C into the soluble, fusible resins by heating it with an excess of phenol.

CONCLUSIONS.

(1) Formaldehyde heated with an excess of phenol and in presence of an acid condensing agent gives fusible, soluble resins, which I call Novolak and which can not be transformed by simple heating in Bakelite.

(2) Novolak is also obtained by heating, under pressure, mixtures of oxybenzyl alcohol and phenol in suitable proportions.

(3) Novolak seems to be a definite chemical compound and not merely a mixture or a solid solution.

(4) Novolak gives various salts, some of which are more or less soluble in alcohol or acetone and which on evaporation give amorphous transparent masses.

(5) Novolak, heated in presence of an excess of formaldehyde in sealed tubes, is transformed into Bakelite, but the latter does not change again to a fusible, soluble resin if heated with phenol.

[1] Baekeland. *Loc. cit.*

(6) The reason why Blumer and DeLaire obtained fusible and soluble resins even when heating phenols with an excess of CH_2O is very probably due to the fact that either some CH_2O escaped during the reaction or remained uncombined, thus altering the proportion of reacting materials.

ACONITE.

By Frank O. Taylor.

Received May 17, 1909.

Despite the wonderful progress achieved in late years in the study of the toxic drugs and of their active constituents, we are yet forced to confess that our knowledge even of the most important of them is far from complete. Notable among these for several reasons is aconite. Known from time immemorial as a drug of exceeding potency, its use and more especially the administration of its various preparations have been attended with uncertainty and even danger because of lack of knowledge as to the quantity and character of active constituents present. To obviate this difficulty, numerous methods of assay have been proposed with varying results, but none of them are free from objectionable features.

The quantitative valuation of aconite and its preparations has been attempted in two ways:

I. Chemical assays, involving two general methods, *viz.*:

(*a*) Estimation of the aconitine through determination of some derived product.

(*b*) Direct estimation of aconitine as such.

II. Physiological assay by two methods:

(*a*) Those based upon effects produced by administration to lower animals.

(*b*) That known by the author's name as the "Squibb Test" (see page 557).

As has been intimated above, there is no perfectly satisfactory method of valuing aconite preparations; and though, for the general pharmacist, chemical assays are to be preferred when available, yet I believe that in this instance the Squibb test is preferable to any of the chemical methods proposed, and in fact is the only one at present which permits of a correct inference as to the therapeutic value of aconite preparations. These conclusions are based upon experience in the preparation of extracts and tinctures of aconite, the constant use of this test and a careful review and comparison of the various assays proposed. There is presented herewith a brief résumé of the literature on the subject and the results of comparative tests. Perhaps many readers will not agree with these conclusions, but it is earnestly hoped that no one who is sincerely interested in this matter will be prevented from making an unbiased comparison through preferences which they may have for some special form of assay.

In reviewing the assay processes detailed criticism has in large measure been purposely avoided, except in case of one or two of the more recent articles, which have emphatically attempted to discredit the Squibb test. As these condemn this test by attempting to demonstrate the accuracy and reliability of chemical assay methods there given, I have criticized them somewhat more *in extenso* in order to demonstrate the fallacy or weakness of the arguments advanced.

Before discussing assay processes and the result of our comparison, it would be advisable to review the statements made by various authorities as to the alkaloids of *Aconitum napellus*, because of the bearing this will have upon the reliability of the assays. As will be seen, there has been a great diversity of opinion, not only as to the number of such active principles normally present in the drug, but also regarding their identity and constitution, though by much laborious research the most important facts regarding aconite and aconite derivatives are now fairly well established.

Alkaloidal Constituents.—After the first isolation of an alkaloid from aconite by Geiger and Hesse in 1833, Groves in 1860 succeeded in obtaining a crystalline alkaloid; Wright in 1875 began his researches on the aconite alkaloids and later Groves and also Jürgens added still more to the knowledge of the aconite alkaloids But the work of all these, while serving well its purpose, was nevertheless erroneous, chiefly because of impurities in the alkaloids examined. Practically all the authoritative work on this subject has been done since 1890, Dunstan and his coworkers contributing by far the most, with Freund and Beck, Ehrenberg and Purfürst, and H. Schulze as the other chief contributors.

The number of alkaloids contained in the root has been variously stated by different investigators. Each of the earlier researches resulted in some difference in results and a new alkaloid would be recorded as occurring in aconite. Such confusion arose from the various names given to practically the same alkaloids, and the same name to different

ones, that it was impossible to correctly list the alkaloids actually present. A. H. Allen[1] gives seven alkaloids as derived from *Aconitum napellus*, but does not state that they all occur naturally in the plant. Thorpe[2] says: "The following list includes the alkaloids about whose existence in the principal species of aconite there seems to be little doubt." Under *Aconitum napellus* he gives "aconitine, isaconitine, homoisaconitine, and aconine." The National Dispensatory (1908, p. 99) gives aconitine, benzaconine (picraconitine or isaconitine, at least in part), aconine and napelline. Dohme in 1895 (28) says: "Aconite root contains the following alkaloids combined with aconitic acid" and then enumerates seven, as follows: "Aconitine, apoaconitine, aconine, picroaconitine, picroaconine, pseudaconitine and pseudaconine, giving formula for each.

Dunstan, speaking to the Pharmaceutical Society (1894), says (21): "We have shown that benzoylaconine and aconine occur in the plant together with aconitine," and the researches of Dunstan and Umney (6) give evidence sufficient for this authoritative statement.

They ascribe the discrepant observations of the previous workers to three sources of error, *viz.*: first, to the confusion of different species; second, to the readiness of decomposition of the alkaloid and, third, to the fact that many determinations of the properties of the alkaloids had been made upon impure material. To avoid these errors, they worked upon fresh tubers which had been specially selected and grown at the suggestion of the British Pharmaceutical Conference.

They first expressed the juice from a large quantity of the root and in this determined the alkaloidal constituents. They found an alkaloid soluble in ether which they crystallized and identified as aconitine and they further obtained a chloroform-soluble alkaloid which could not be crystallized and which seemed to be identical with aconine. Continuing their work upon the expressed roots, they obtained two similar alkaloids together with indications of two other non-crystalline alkaloids, and proved the first two to be aconitine and aconine. A careful study of the report of their work will show remarkable absence of any source of error, and whatever may have been later determined about the constitution of these alkaloids, there seems to be no escape from accepting the conclusion that there exists in the green aconite root more than one alkaloid.

Dunstan and Ince (2), 1891, describe the properties of crystalline aconitine and state that upon hydrolysis it yields benzoic acid and a second alkaloid, aconine, which reaction had also been noticed previously by Wright and Luff. In 1892, Ehrenberg and Purfürst (8), working upon the same hydrolysis, stated that they found produced benzoic acid, another acid which was identified as acetic, and methyl alcohol, together with aconine. Their researches also go to show the presence of four methoxyl groups. While they found benzoic and acetic acids produced by hydrolysis, they failed to arrive at proper conclusions regarding the structure of the alkaloid, the finding of acetic acid being merely incidental. About the same time Dunstan and Passmore (7), 1892, published some extended researches upon the same subject, in which they describe the properties of pure aconine and its crystalline salts, and note the formation of benzoic acid during the hydrolysis of aconitine, but find no methyl alcohol produced and do not mention a second acid.

Shortly after this, Dunstan and Harrison (9), 1893, took up the investigation of one of the other alkaloids, which Dunstan and Umney had previously obtained and called napelline. From their investigations they found that on hydrolysis benzoic acid and aconine were produced as in the case of aconitine and, from the large amount of experimental data which they gave, decided that it was of the same formula as aconitine and hence designated it isaconitine. In 1893, Dunstan and Carr (11) reported to the Chemical Society that, from some experiments they had made, aconitine when undergoing hydrolysis seemed first to change into isaconitine, but they did not at the time recognize the nature of the change. The following year Dunstan and Harrison (13) reported an investigation of the picraconitine of Wright and determined it to be identical with isaconitine, that is, benzoylaconine.

On January 17, 1894, Dunstan and Carr (14 and 15) transmitted a communication to the Chemical Society, which was published in the Proceedings of January 27th and which gave in brief the result of some of their researches upon the effect of heat upon aconitine and some of its derivatives, in which they show for the first time that isacontinei is but a decomposition product of aconitine and arrived at the conclusion that aconitine is acetyl-

[1] "Com'l Organic Analysis." Vol. III, Pt. 2, 201.
[2] "Dict. of Chem." Vol. III, p. 905.

benzoylaconine. On February 19, 1894, Freund and Beck (16) published in the *Berichte* the result of their researches upon aconitine from which they deduce the same conclusion, but they assign a different formula to aconitine and give it a different melting point. The full papers of Dunstan and Carr were published a short time later in the *Journal of the Chemical Society*. From both of these researches it is shown that aconitine is acetylbenzoylaconine, that isaconitine, formerly supposed isomeric with aconitine, was in reality benzoylaconine; that is, it was produced from aconitine by hydrolysis with the separation of acetic acid and that, as the final products of hydrolysis, aconine and benzoic acid will be obtained. The claim for priority of this discovery was a source of heated discussion between Freund and Dunstan, but into the merits of which there is no necessity for us to enter. For the details of this controversy and the basis of it, references may be made further to Dunstan (17), Freund and Beck (18), Dunstan and Carr (23) and Freund (26), where much additional information not given in the above-mentioned papers will also be found.

More recently H. Schulze has attacked the problem of the constitution of aconitine (54 and 55). A long series of analyses of specially purified aconitine, its hydrobromide, and its salt with gold chloride tend to confirm the formula of Freund and Beck, $C_{34}H_{47}NO_{11}$, though Schulze points out that his results agree equally well with the formula $C_{34}H_{45}NO_{11}$ which he suggests may be the true one, at any rate the results are in the main against that of Dunstan, $C_{33}H_{45}NO_{12}$. His analyses of aconine hydrochloride are further confirmatory of these deductions.

In his second paper he confirms the presence of four methoxyl groups as stated by Freund and Beck and in addition demonstrates the presence of a methyl group united with the nitrogen atom. He also produces triacetyl aconitine, confirming the work of Dunstan and Carr and demonstrates that the hydroxyl groups so replaced are of an alcoholic rather than phenolic character. Later in the same year (1905) Dunstan and Andrews published two papers (59 and 60), regarding the alkaloids of *Aconitum chasmanthum* and *Aconitum spicatum* and at the same time there appeared an article by Dunstan and Henry (61), giving a brief review of the various species of *Aconitum* and their alkaloids. Also a comparison of the characteristics of aconitine from *Aconitum napellus* as obtained from English grown tubers and from the German plants. The distinction is so marked that Dunstan suggests as a highly probable conclusion that the aconitine upon which the earlier researches, conducted under his direction, were made, and that used by later German investigators are from different varieties of *Aconitum napellus*, at present not so considered. This is the more probable in view of the varieties of Indian aconite now known, which were formerly counted as one species.

During 1906 Schulze contributed still more toward the solution of this question (63 and 64). In the former of these two papers he enters into a complete historical survey of work on aconitine and aconine from *Aconitum napellus*, and a discussion of their formulae. In the latter paper are recorded the experimental details on which much of the prior paper was based. He also endeavors to controvert Dunstan's theory of the dissimilarity of English and German *Aconitum napellus* by citing a crystallographic examination of the German aconitine and showing its exact likeness to the crystals obtained by Dunstan and examined by Tutton (3).

These researches are practically the limit of our chemical knowledge of aconite at the present time and from them there seems to be no question that aconitine, benzoylaconine and aconine exist as such in aconite. Of these, numerous decomposition products may be obtained, but these three alone are probably the only natural alkaloids of the plant. Accepting the formula of Freund and Beck, we may then show the relationship between these three alkaloids and what we know of their constitution as follows:

$$\underset{\text{Aconitine}}{C_{34}H_{47}NO_{11}} + H_2O - CH_3.COOH + \underset{\text{Benzoylaconine.}}{C_{32}H_{45}NO_{10}}$$

$$\underset{\text{Benzoylaconine.}}{C_{34}H_{42}NO_{10}} + H_2O = C_6H_5.COOH + \underset{\text{Aconine.}}{C_{25}H_{41}NO_9}.$$

There being four methoxyl groups in aconitine, the constitution of this alkaloid, so far as we know it, is

$$C_{20}H_{21}O_2NCH_3(CH_3O)_4(OH)_3(CH_3.CO)(C_6H_5.CO).$$

The above citations point to the conclusion that aconite tubers either green or dried contain basic bodies other than aconitine. No one has, to my knowledge, offered any evidence to the contrary. It will be well for the reader to keep in mind this fact when reading the criticism on the solubility of the alkaloidal bases in the solvents employed in assays.

Properties of the Alkaloids.—Aconitine may be crystallized from ether in colorless or slightly yellowish prisms belonging to the rhombic system and possessing a marked tendency to a tabular form. For a description of their crystallographic characters, Tutton (3) and Schulze (64) may be consulted. It is almost insoluble in water and petroleum ether, soluble in alcohol and ether, and very soluble in chloroform; the exact solubility in these solvents is variously stated.

Of the numerous formulae given for aconitine, but two of them are widely accepted as being authoritative, namely, that of Dunstan as $C_{33}H_{45}NO_{12}$ (642.52) and that of Freund and Beck, $C_{34}H_{47}NO_{11}$ (640.55), with that of Schulze, $C_{34}H_{45}NO_{11}$ also probable, while a fourth, advocated by Ehrenberg and Purfurst as $C_{32}H_{47}NO_{11}$ (612.73), has not received substantiation by the latter work of Freund, Dunstan and their co-workers and Schulze. Pictet says: "The composition of aconitine has not been fully established. The two most probable formulae for the alkaloid are, however, $C_{33}H_{45}NO_{12}$ (Dunstan) and $C_{34}H_{47}NO_{11}$ (Freund and Beck)."

For all our calculations, the formula of Freund and Beck, which has a molecular weight of 640.55 (H = 1), has been accepted.

The melting point usually recognized as quite characteristic for organic substances is variously given. Dunstan and Ince (2) give it as 188.5°, while Freund and Beck (16) state that 197°–198° is the true melting point. Schulze (54) reports the melting point of a sample of Merck's aconitine as 195° and of a specially purified sample as 197° and later (63) that of aconitine recrystallized from alcohol as 197°–198°. We may notice in this connection that the firm of Merck & Co. (*Merck's Index*, **1902**, p. 17) give "about 190°" as the melting point which is much nearer to the former figures. My experience has been that the melting point is very gravely affected by the conditions of the determination; the same crystalline aconitine may be made to give melting points varying a number of degrees by a difference in manipulation.

Aconitine is extraordinary in the fact that its alcoholic solution is strongly dextro-rotatory, $[\alpha]_D$ +11° while its salts are still more powerfully laevo-rotatory, $[\alpha]_D$ —30° to —31°. In this respect, the aconite alkaloids differ from all other important vegetable alkaloids.

Benzoylaconine is a non-crystalline alkaloid which when pure appears as a colorless, transparent varnish, which is easily powdered and melts indefinitely near 125°, is slightly soluble in water, *readily soluble in alcohol or chloroform and also in ether.* The alcoholic solution is dextro-rotatory, about $[\alpha]_D$+4.4 and its salts rotate up to —30° to the left. It is bitter in taste and *does not produce the tingling sensation on the tongue, so characteristic of aconitine.*[1]

Aconine in the pure state is a colorless, gum-like mass which is not crystallizable and melts at 132° without decomposition, is very soluble in water or alcohol, slightly in chloroform, insoluble in ether and light petroleum. It is, like the other aconite alkaloids, dextro-rotatory, about $[\alpha]_D$ +23 while its salts are laevo-rotatory. It is bitter in taste and, like benzoylaconine, produces no tingling sensation on the tongue.

Some pertinent facts worth remembering appear above. First, only aconitine forms crystals, benzoylaconine and aconine both existing as varnish-like bodies. Second, that of the three, *only aconitine* produces a tingling sensation on the tongue.

Physiological Action of the Alkaloids.—Cash and Dunstan (39) have carefully investigated the physiological action of aconitine and some of its allied alkaloids, their paper on "The Pharmacology of Aconitine, Diacetylaconitine, Benzaconine and Aconine" being a very complete one, covering over 150 pages of the *Philosophical Transactions* (1898, **190,** 239), a thorough abstract being published in the *Proceedings of the Royal Society* as above noted.

They tested the alkaloids with regard to the following points:

"1. Their effect upon the blood pressure, pulse and respiration of anaesthetized cats.

"2. Their general effect and especially their action upon temperature and respiration of rabbits, and (occasionally) of guinea-pigs.

"3. Their general toxic action upon the following organs and functions of other animals, separately examined: circulation, respiration, spinal cord, reflex, motor and sensory nerves, and muscles.

"4. Their lethal dose towards some or all of the various animals employed."

They found that the toxic action of benzoylaconine was very much less than that of aconitine and also different in character. Aconine was shown to be still less active and the source of the powerful toxic action of aconitine proved to be

[1] See Dunstan and Harrison, "On Isaconitine," *Jour. Chem. Soc.*, **1893**, p. 443

the acetyl group present. The addition of a second acetyl group, producing diacetylaconitine, reduced the toxicity but did not materially modify its nature.

In their conclusions they have this to say of benzoylaconine:

"On the heart, indeed, it acts to some extent as the antagonist of aconitine, ... so that in a certain measure it is observed that benzaconine behaves as an antidote to aconitine poisoning though not so effectively as atropine. This is a point of considerable practical importance when it is remembered that benzaconine occurs to a variable extent with aconine in *Aconitum napellus*, from which the ordinary medicinal preparations are made."

As to the action of aconine physiologically, they conclude that it "is so far from being a heart poison that it may be ranked as a general cardiac tonic, and in virtue of this action as the antagonist of aconitine. In a much greater degree than benzaconine it is an antidote to aconitine, so much so that we have found that the administration of aconine is successful in averting, in small animals, the effect of the lethal dose of aconitine."

As the illustrative of the comparative toxicity of the four alkaloids tested, the lethal dose for the cat as given by Cash and Dunstan, expressed in fractions of a gram per kilo body weight, is given below:

Aconitine	0.000134
Diacetylaconitine	0.004 to 0.005
Benzaconine	0.245
Aconine	0.16 to 0.4

Difficulty and Value of Assay.—From consideration of the foregoing description of the chemical and physiological properties of the aconite alkaloids, the conditions and characters of the theoretically correct assay may be deduced, and at the same time, the sources of error in various proposed methods of assay become readily apparent. *Because of the antagonistic action of the three alkaloids, a method of assay* which is correct must determine aconitine *available for therapeutic* action. The most favored assay at present is that depending upon an estimation of the ether-soluble alkaloid, but benzaconine is also soluble in ether and aconine, though stated to be insoluble, is not completely so, its solubility being probably increased by admixture with the ether-soluble alkaloids. From an examination of the solubilities of these alkaloids (see page 552), it is apparent that their separation presents peculiar difficulties. It will be shown that the estimation of the ether-soluble alkaloids of aconite is not an accurate criterion of the physiological activity of the preparation assayed, both from the reasons given and for others yet to be mentioned. In this connection, a discussion which occurred at the meeting of the Pharmaceutical Society, February 11, 1896 (33), is of interest. Dr. Attfield remarked on the necessity of determining aconitine alone and the possible usefulness of a determination of total alkaloids. Prof. Dunstan said: "With regard to Prof. Attfield's remarks, he (Prof. D.) ought to make it clear that it was quite easy to determine the total alkaloids, but it was absolutely useless, as he had indicated; much more so when in the case of nux vomica to determine the strychnine and brucine together. Brucine had in some respects a similar action to strychnine, but in the case of aconitine, as far as he could make out, nothing but the aconitine was of the slightest value, and therefore the determination of the total alkaloids would be entirely misleading."

Aside from the natural existence of three alkaloids in the drug, we have yet to consider the possibilities of decomposition products, which may be present from various causes. While the tuber itself may vary greatly in physiological activity, its preparations will be subject to still greater variation according to the care used in preparing them. For example, a fluid or solid extract which has been accidentally exposed to excessive heat will have the aconitine largely decomposed with the consequent loss in its therapeutic efficiency, and the same effect is liable to be the result of aging, fermentation in the drug, and similar causes. A method of assay which will not show the true therapeutic value of any finished preparation is not one to be relied upon, for it is in such cases as this that the greatest danger from variation in strength may occur. Furthermore, an accurate method of assay should certainly be capable of estimating the actual amount of aconitine present in commercial specimens of the alkaloid, a result which cannot be accomplished by the use of ether as a solvent, since the amorphous aconitines of commerce are far more soluble in ether than is proportionate to their potency. The intention of the chemical assay of a drug or drug preparation is to establish its therapeutic value which may have been altered by use of poor drug, intentional adulteration or carelessness, and an assay which is inapplicable in the face of any one of these conditions is practically valueless, or at

least not to be utilized if something better is available.

Methods of Assay which Have Been Proposed.

I.—Chemical.

A.—*By Estimation of Some Derived Product.*

1. *Estimation of Acetic Acid Produced by Hydrolysis.*—Dohme (28) detailed the results of his attempts to utilize the process for estimation of aconitine by determination of acetic acid produced by hydrolysis, as suggested by Dunstan and Carr (*Jour. Chem. Soc., Transactions*, **1894**, 292). His conclusions are stated as follows: "These results deduced from the amount of acetic acid neutralized by the standardized alcoholic potash solution, just given, show conclusively that this is not a reliable method of assay."

Dunstan and Tickle, in 1896 (29), published an account of an endeavor to apply this method to the estimation of aconitine in the drug and its preparations. They obtained results which were markedly too high, and after recording their experiments, concluded by saying: "We have spent considerable amount of time in trying to definitely ascertain the cause of these high results, but so far without complete success....... Whatever the explanation of the fact may be, it is clear that at present, the determination of the acetic acid furnished by the total alkaloids of *Aconitum napellus* cannot be taken as a basis for the calculation of the quantity of aconitine." They say further, in emphasizing the necessity of estimating aconitine alone, that "until a satisfactory process for the estimation of aconitine in the total alkaloids has been found, no progress can be made in standardizing galenical preparations from the plant."

2. *Estimation of Benzoic Acid from Hydrolysis.*—In the course of the experiments made by Dohme, previously referred to (28), he also employed this method. Saponifying the aconitine with alcoholic potash, collecting the benzoic acid produced, on a weighed filter and weighing, he obtained results which were of doubtful value. Among other conclusions which he reaches, he says, "that until we know more about the remaining alkaloids and constituents of aconite root, no reliable method of assay of the root or of the active principle, aconitine, can be devised and that neither of the methods above tried are to be stated as reliable."

A. H. Allen ("Com. Org. Anal.," Vol. III., Pt. 2, p. 234) advocates the same method, the origin of which may, however, be attributed to Alder Wright. Such analytical results as he gives are rather discrepant.

3. *Estimation by Means of Mayer's Reagent.*—This method, formerly well thought of as a method of alkaloidal estimation, has become obsolete for aconitine as well as for other alkaloids. Its accuracy was questionable even for estimation of total alkaloids and for estimation of aconitine alone, it is useless.

4. *Iodometric Estimation.*—The production of the periodide of aconitine and estimation of iodine, so combined, has been used by Prescott and Gordin (38) for the assay of aconite. They obtained a triiodide ($C_{33}H_{45}NO_{12}.HI,I_2$) and a heptiodide ($C_{33}H_{45}NO_{12}.HI,I_6$),[1] but their experiments were not sufficiently extended to enable them to give definitely their opinion as to the value of this method for the quantitative estimation of aconitine. It is manifest that iodides of other alkaloids present would also be formed at the same time.

In 1900, Kippenberger (42) made an attempt to apply the formation of the iodides to the assay, but concluded that the process was not well adapted to this purpose. It appears, therefore, that this method also is not to be seriously considered for the determination of aconitine.

5. *Silico-tungstic Estimation.*—More recently still, Ecalle (47) has published another indirect method for aconitine estimation. He makes use of the property which many alkaloids possess, of forming a definite compound with silico-tungstic acid. The method involves the previous separation of the ether-soluble alkaloids, their subsequent conversion into silico tungstate and then by ignition, silico-tungstic acid is obtained and weighed. From this weight, calculation of the amount of aconitine may be made. I have not made special trial of this method, but it is evident that it will estimate the same alkaloids which are estimated by the ether extraction and titration method, and consequently is open to the same objections.

B. *Assay by Extraction of Alkaloid and Determination by Weight or Titration.*—By far the greater number of methods come under this class, though they vary among themselves in the solvent which is used and also in the details of manipulation. The most natural thing to do was to apply some modification of the commercial methods of extraction to the assay of the drug. Remarkably different results have been obtained by different investigators. Alder Wright believed the root

[1] They employed the formula of Dunstan

to contain about 0.07 per cent. total alkaloids. Dragendorff found alkaloids ranging from 0.054 per cent. to 0.0327 per cent. in the fresh root. Hager obtained from 0.05 to 0.4 per cent. of crystalline alkaloid and total alkaloids to the extent of 0.64 to 1.25 per cent. Richards and Rogers (5) report the anomalous results of 0.14 per cent. crystalline aconitine in the dried tuber and 0.71 per cent. in the green drug, thus indicating a tremendous decomposition of aconitine in process of curing, to produce results in the proportion of 71 to 14 and yet compensate for shrinkage in weight through drying. Keller (22) finds from 0.87 to 1.23 per cent. of (mixed) alkaloid. Dohme (43) says: "I have found as high as 0.96 per cent. total alkaloids." Stevens (54) obtained from different grades of drug, 0.084 to 0.7 per cent., which is presumed to be aconitine. Beckurts reported (49) 0.61 to 0.71 per cent. denominated "alkaloid" but, which from the nature of the solvent used must have been mixed or total alkaloids. With these last three statements my own observation agrees.

Barring variations in manipulation and details of purification of the product of the assay, the numerous methods fall into four groups, namely, (1) those which use amyl alcohol for the extraction of the alkaloids from the drug, (2) those which employ chloroform for the same purpose, (3) those in which a mixture of ether and chloroform is applied to the extraction of the alkaloids, and (4) those in which the ether alone is used throughout the assay.

Proceeding on the supposition that aconite tubers contain at least three alkaloidal bodies, and this assumption is warranted by a review of the evidence cited on pp. 549-50, it logically follows that we may dismiss from consideration all assay methods which employ amyl alcohol, chloroform or a mixture of ether and chloroform as extracting or solvent agents, *without final purification through ether*. The drug and its preparations contain basic bodies other than aconitine and these are dissolved by the solvents above mentioned and hence estimated as aconitine or as total alkaloids, which is equally useless for therapeutic purposes. The use of ether as the sole solvent or for final extraction of aconitine from mixed total alkaloids is fallacious because the secondary alkaloids or decomposition bodies are also soluble to a greater or less degree in ether; in other words, the result is not pure aconitine.

The following four methods represent the various assay processes proposed by different authors, similar individual methods differing only in detail; two of them rely upon solution in ether to quantitatively extract aconitine. A fluid extract of the drug made in the usual manner was used as a starting point in all cases.

Method I.—Evaporate 20 cc. of the fluid extract (or in the case of the drug, the extract made from it) at a temperature of 40° C. until all the alcohol is removed; mix the residue thoroughly with 20 cc. of water, add 100 cc. of amyl alcohol, shake well and add 20 cc. of 5 per cent. solution sodium bicarbonate, and shake well for two hours. Filter off 50 cc. of the amyl alcohol solution and extract with 20 and 10 cc. of 1 per cent. sulphuric acid, washing finally with 10 cc. of water. Render this acid solution alkaline with ammonia and extract with a mixture of equal parts ether and chloroform. Evaporate and treat residue twice with ether, evaporating after each addition to remove ammonia. Dry in desiccator over sulphuric acid. The residual alkaloid may be weighed and subsequently titrated.

Method II.—Evaporate 10 cc. of fluid extract at 40° C., or the extract from the equivalent quantity of drug, until all alcohol is removed. Dissolve in 20 cc. of water slightly acidulated with sulphuric acid, filter into a separatory funnel, make alkaline with ammonia, and extract with chloroform. This chloroformic solution is extracted with 1 per cent. sulphuric acid as in the preceding. Render the acid solution alkaline with ammonia, extract with chloroform and continue the assay as in Method I.

Method III.—This differs from Method I only in using for the first extraction a mixture of equal parts ether and chloroform, and for the final extraction ether alone.

Method IV.—Evaporate 10 cc. of fluid extract at 40° C., or equivalent quantity of extract from the drug, to remove alcohol, dissolve in 10 cc. of 1 per cent. sulphuric acid and filter into separatory funnel, washing out evaporating dish and filter thoroughly with water. Render this acid solution alkaline with ammonia and extract four times with ether. The ethereal extract is evaporated to dryness and is then weighed and titrated.

Titration in every case is accomplished by dissolving the residue in 5 cc. of $N/10$ sulphuric acid with the aid of a little ether, evaporating off the ether and titrating excess acid with $N/50$

alkali, using cochineal as the indicator. Each cc. of $N/50$ acid consumed by the alkaloid corresponds to 0.012811 gram of aconitine.

In obtaining the subjoined results, portions of a fluid extract made from good quality of aconitine tuber, by process of cold repercolation, were employed. The fluid responded distinctly to the Squibb test at a dilution of 1 part in 700, showing that it was of good quality. Duplicate assays by each process were now made on this fluid, the alkaloid finally obtained being dried *in vacuo* over sulphuric acid and weighed, titration being applied also after weighing, in order to get a comparison of results. Besides assaying the fluid, the requisite amount for the assay was put in an air bath at 100° and heated at this temperature for exactly two hours. On this, duplicate assays were made as on the original fluid, both by weight and titration. Squibb tests were likewise used on similarly heated samples, and at a dilution of 1 : 80 no test could be obtained. The test was not carried to a greater concentration but this shows that the amount of available aconitine was reduced to less than 12 per cent. the original amount. The record of assays appended in tabular form shows the results obtained.

Assays of F. E. Aconite by Four Methods Given.

				Percentage.	
				By weight.	By titration.
I.	A	Evaporated below 50° C	1	0.468	0.477
			2	0.475	0.477
	B	Evaporated for 2 hours at 100° C	3	0.434	0.387
			4	0.507	0.477
II.	A	Evaporated below 50° C	5	0.504	0.555
			6	0.515	0.555
	B	Evaporated for 2 hours at 100° C	7	0.418	0.439
			8	0.416	0.452
III.	A	Evaporated below 50° C	9	0.410	0.335
			10	0.408	0.335
	B	Evaporated for 2 hours at 100° C	11	0.266	0.232
			12	0.319	0.245
IV.	A	Evaporated below 50° C	13	0.551	0.438
			14	0.455	0.438
	B	Evaporated for 2 hours at 100° C	15	0.591	0.323
			16	0.597	0.387

The assay with chloroform gives, as would be expected, the highest results; the one assay with a higher result by Method IV is probably the effect of some error in manipulation as it will be seen by examining Table II, that this method gives quite uniform results in accord with the lower figure here when it is used on the unchanged fluid extract. The results by titration show always concord between duplicates, but in the majority of cases do not agree with the results by weight, sometimes, as in Method II, showing more aconitine than can possibly be present if all the residue were the pure alkaloid, while in other cases, such as Method III, showing much less than by weight. But it is in the assays made on heated fluid extract that we find the most erratic results. Here the duplicates, either by weight or titration, agree closely in but two instances and in only one case (Method III, 11 by weight) is there an indication of a lowering in strength of more than 30 per cent., while in Method I, 4 by titration, no change is shown. The other assays give evidence of less than 30 per cent. reduction in aconitine. But the Squibb test, which indicates therapeutic value by reason of being based on a physiological effect of aconitine peculiar to that alkaloid, showed that there could not be as much as 12 per cent. of the original amount of that alkaloid available; the assays, therefore, are in no case as close to the truth as within 50 per cent. of the original aconitine strength. As a result of above assays, Method IV was selected as being typical of the class and as being probably the best in all respects. With minor variations it is identical with the process given in the U. S. P., 8 R., which I shall use as a basis for comparing the chemical assay and the Squibb test (see page 559).

II.—Physiological.

A.—*On Animals.*—Cash and Dunstan (39) have made by far the most extended researches on the pharmacology of aconitine so far published, but in all their experiments, no mention is made of an attempt to use the physiological activity as a method of assay. Stevens (51) records, however, some experiments with this end in view, they being based upon the toxic dose for a frog. His results by this means were decidedly erratic and not promising of accurate results. Mandelin[1] contributes a lengthy article in an endeavor to elucidate in some measure the "aconitine question" and among other things records (p. 781) some experiments on frogs from which he concludes that they are not suited for testing aconite as the results were so variable. It seems that this means of estimating the activity of aconitic preparations has been but little attempted and so, though published results have not been encouraging, it is possible that the method may be made to yield

[1] *Pharm. Jour.* [3], **16**, 705, 727, 781 and 801

better results if used on a higher order of animals than frogs.

B.—*The Squibb Test.*—Many years ago the late Dr. E. R. Squibb awoke to the fact that aconite preparations were exceedingly toxic and also that they varied much in therapeutic activity. He undertook an investigation with the idea of determining the relative doses of the various derivatives of this drug and of estimating their activity. Chemical assay methods not being sufficiently developed at that time to warrant a resort to this means, and influenced no doubt by a desire to formulate a test which could be readily applied by either the pharmacist or physician, he devised a test based upon that peculiar property which aconitine has of producing a tingling or numbing sensation upon the tongue and mucous surfaces of the mouth. The author did not make any extravagant claims as to its quantitative value, but he did believe that it would indicate preparations even slightly deficient in strength. In *Ephemeris*, **1**, 136 (1882–3), he says of the fluid extract: "Each parcel of it bought by the pharmacist or the physician should be tested, and if one-tenth of a minim of it, diluted with a fluid drachm of water and held in the mouth for one minute, does not give the aconite impression within ten minutes, the parcel should be rejected, or its strength should be obtained and doses increased accordingly."

This test is so simple and requires so little time and withal affords such definite conclusions that one cannot but marvel that those chiefly concerned displayed so little interest in it. Dr. Squibb had long before this time established a reputation among scientific men for the accuracy and reliability of his work and he was not given to jumping at conclusions. Yet it appears that during the 26 years which have elapsed since its publication, physicians and pharmacists alike have forgotten it. The *Pharmaceutical Era*, **1888,** pp. 64 and 104, published the results of some comparative applications of this test and concludes that when applied by those who have some experience, the results are fairly reliable, and of value in detecting a badly deteriorated extract or fluid. F. A. Thompson[1] published data calculated to demonstrate its practical value in the laboratory. L. F. Kebler (48) reports assaying several samples of aconite drug by gravimetric, volumetric and Squibb's methods and concludes that only the last is of value. A. B. Lyons (68) after comparison of the U. S. P. assay and the Squibb test concludes that the chemical assay is not reliable and advocates the Squibb test. His conclusions are quoted *verbatim* on page 560.

The Squibb test has been used in the laboratories of Parke, Davis & Company for more than twenty years and it has been checked against itself on diluted fluids and concentrated fluids times without number, and has always been found concordant, easy of manipulation, and accurate to a degree certainly never claimed by its originator. While for close estimates, it requires the experience gained by a few trials on material of known strength, its mastery offers no difficulty to any average pharmacist or chemist, and certainly for distinguishing a good fluid extract from a mediocre one it is easily available for every one who can measure a dilution.

While this test is certainly not perfect by any means, and perhaps the near future will yield a reliable chemical assay, yet every one proposed up to date has been open to the criticism of estimating total alkaloids, or at least a very impure aconitine, and consequently are not so accurately an indication of medicinal value as the Squibb test.

The test as published in *Ephemeris*, **1**, 126 and **3**, 293, may be tersely stated as follows:

SQUIBB TEST.

Dilute the fluid extract (other derivatives in proportion) in such proportion that 1/10 minim will be contained in 1 fluid drachm of water. Rinse out the mouth well to free the surfaces from mucus and saliva and hold the above one drachm of dilution in the anterior part of the mouth for exactly one minute and then discharge it. A distinct aconite (tingling) sensation should be perceived within 10 to 15 minutes.

The above dilution is in proportion of 1 part of fluid extract to 600 parts water. In laboratory practice, it is better to require the fluid extract of the drug to respond in dilution of 1 in 700, the fluid extract of leaves, 1 in 100, the extract of root, 1 in 3000, and aconitine, 1 in 500,000. In the application of the test, dilute 10 cc. of the fluid or one gram of the extract to the calculated volume, using water acidulated with acetic acid in the first step and pure water for the final dilution.

Criticism of the Squibb Test.—As intimated above, little attention has been devoted to this test by pharmaceutical writers. Thompson published his results twenty years ago. More recently, reports on the alkaloidal assay of aconite by chemical

[1] *Druggist Bull.*, **1889**, page 108.

methods have appeared from time to time, but with three exceptions, those of Stevens, Dohme, and Lyons, such articles have not referred to the Squibb test at all. As the article by Stevens endorses the chemical assay and those of Dohme (43–44) are directed against the Squibb test and incidentally against the whole scheme of physiological tests, they will be reviewed rather more critically than any others. An examination of Dohme's two articles, published in the *Druggists' Circular*, 1900, pages 69 and 133, shows that he quotes no comparative results at all, but relies wholly on showing that his chemical assay estimates aconitine quantitatively and that consequently any other assay is needless; the Squibb test is dismissed with the statement, "As soon as the personality of the individual is brought into the analysis, then idiosyncrasy must kill all accuracy of result. The tongue does this effectually for Dr. Squibb's assay, and the lower order of vertebrates for the so-called physiological method."

Referring to the article in the *Druggists' Circular*, **1900**, p. 69, among other statements he says: "At any rate, as I have before stated, aconite can be assayed chemically if the proper method and precautions are used, and the results below prove it. The work, however, is not finished as yet, as I propose to show that the product I get as the result of the assays, is aconitine, unimpaired in its physiological activity. That it is aconitine, I have shown by a chemical examination of some of it when recrystallized." The query naturally presents itself: If the product he obtains by his assay is aconitine, why is it necessary to recrystallize it before determining its identity? What is the remainder of his product which does not recrystallize and which consequently is not submitted to the chemical identity tests? He further says: "After the alkaloidal product I have titrated as aconitine and found to be aconitine chemically shall have been shown to yield all the therapeutic effects of aconitine, the claimants of the physiological test necessary for aconite will have no ground to stand on......etc." It is manifest that a mixture consisting of only 80 or 90 per cent. aconitine will give the therapeutic effects of aconitine, but Dohme does not record any therapeutic tests.

The assay process and results recorded by Dohme are as follows:

"The proportions of ingredients of the assay were:

For Root.—Drug, 12 grams; ether, 90 grams; chloroform, 30 grams; ammonia (0.96), 10 grams; water, 20 grams.

For Leaves.—Drug, 25 grams; ether, 100 grams; chloroform, 25 grams; ammonia (0.96), 10 grams; water, 50 grams.

Operations.—Filter off 100 grams or an aliquot portion by weight, each 10 grams in case of root, and each 5 grams in case of leaves representing 1 gram of drug. Extract with 5 per cent. sulphuric acid, make alkaline with ammonia and extract with a mixture of equal parts of chloroform-ether at a temperature not exceeding 50° C. and if possible less, and titrate the residue with centinormal potassium hydroxide, after dissolving it in the cold with a definite amount of decinormal sulphuric acid.

The residue in these assays presented the usual appearance of almost colorless varnish with a tendency to crystallization. The results follow:

		Per cent.
Aconite root	*a*	0.620 total alkaloids.
	b	0.619 " "
Aconite leaf	*a*	0.210 " "
	b	0.205 " "

The author himself denominates the products obtained by his assay "*total alkaloids*" and even if he did not, it is perfectly patent that if this drug contains basic bodies other than aconitine they will be extracted by his chloroform-ether menstruum. Yet in a second article ("The Product of the Aconite Assay," Dohme and Englehardt, *Druggist Circular*, **1900**, p. 132), which is practically a continuation of the one just quoted, we have this assertion: "To place the reliability and trustworthiness of the assay beyond the question of a doubt, there remained the proof that the product of the assay was aconitine and not any of its decomposition products. In other words, is the resinous-looking residue left after the evaporation of the ether-chloroform extract, aconitine, or is it not?"

This is just the question to be answered, and if the author cannot prove the affirmative, his whole contention falls of its own weight and with it his condemnation of physiological assay process. Let us see what he says further: "We examined the products obtained by both assay methods employed in the paper referred to, and found that both of them were aconitine, although both were of different purity." If both or either were aconitine, how could they be impure at all? If they were aconitine why did he denominate them "total alkaloids" in the article published previously and quoted *verbatim* on this page. To prove that the assay product was aconitine, he now made an assay extraction of 500 grams of the

same drug, "using larger quantities merely of all solvents, etc., required by the assay." The author does not apply chemical identity tests to the varnish-like residue obtained by the assay method to prove that it is aconitine, but "This product was in each case dissolved in ether and allowed to evaporate slowly. The result was a good crop of crystals possessing a white color, which were dried between bibulous paper and then tested as to their melting point." Here is a quantitative extraction of mixed or total alkaloids pronounced aconitine because, on further treatment with ether and crystallization from the same, some crystals of aconitine were obtained. If the "varnish-like" residue quantitatively extracted by ether-chloroform is aconitine, why extract by ether? Yet he decides that because from an etheral solution of this varnish-like mass, some aconitine crystals are obtained, *the whole mass is aconitine*, for he says, after taking melting points of the ether-extracted crystals, "This indicates conclusively, in fact it proves, that by Method II at any rate, and to a very great extent by Method I as well, the product of the aconite assay is aconitine."

This does not indicate conclusively that either method estimates aconitine alone, but it does prove that this assay determines total alkaloids, containing aconitine, but that to estimate *aconitine* quantitatively, this assay is certainly of little use, and misleading. If this method was intended as an assay for total alkaloids it would deserve consideration, though it is conceded by all who have investigated the subject that the content of total alkaloids is not an index to the therapeutic value of aconite or its preparations.

The method published by Stevens (52) is based upon the decision reached by later investigation, that if aconite can be assayed by chemical methods, it is necessary to resort to extraction by ether to exclude, in so far as may be possible, the basic bodies with which aconitine is associated. This is undoubtedly an improvement on the Keller process employed by Dohme, which extracts mixed or total alkaloids by the ether-chloroform solvent, but is open to the criticism that while the substance estimated consists largely of aconitine, yet it always contains varying proportions of the associated bases. That other alkaloidal bases are normally present in both the green and dried tubers, is sufficiently demonstrated by the evidence quoted on pages 549-50. Benzoylaconine is soluble in ether as is to a small degree aconine. The amorphous aconitine sold by prominent manufacturing chemists is almost as readily soluble in ether as the crystalline aconitine, yet the former is only about one-tenth to one-fifteenth as active as the latter. It is certainly possible to produce ether-soluble bases, not aconitine, in aconite by artificial means and it is quite probable that such are produced by oxidation, fermentative processes or other treatment to which this drug or its derivatives are or may be subjected. That such bodies can be found in pharmaceutical preparations is shown on page 556, and Stevens evidently found this true as he says in referring to the effect of heat: "The results of experiments on extracts proves that no reliance can be placed upon a chemical method of assay when applied to any preparation of aconite long subjected to heat." I have found in a number of cases that the careless use of heat in the drying of aconite extracts resulted in the almost total destruction of the aconitine, as indicated by the Squibb test, though the ether assay process yielded results indicating a full strength extract; this fact is also demonstrated experimentally (see page 561).

Stevens' assay is as follows, being almost identical with the U. S. P. process:

ASSAY METHOD FOR ACONITE.

Place ten grams of aconite in a flask; add 75 cc. of a mixture of alcohol, 7 volumes, and water, 3 volumes; then agitate for four hours.

Place a plug of cotton in the bottom of a small percolator, 25 mm. in diameter, and add the mixture. When the liquid has all passed through, percolate with the same menstruum until 150 cc. of percolate are obtained. Pour the percolate on an ordinary dinner plate and mix with five grams of powdered pumice stone, then evaporate to dryness at a temperature not exceeding 60° C. Add 5 cc. of N/10 sulphuric acid and 10 cc. of water. When the extract is dissolved, filter into a separator. Wash the plate and filter with about 40 cc. of water. Add 25 cc. of ether and 2 cc. of ammonia water and agitate for five minutes. Draw off the lower layer into a flask and filter the ether into a beaker. Return the contents of the flask to the separator, add 15 cc. of ether and agitate three minutes. Draw off the lower layer into the flask and filter the ether into the beaker. Repeat with two other portions of 10 cc. each of ether. Evaporate the ether to dryness and dissolve the residue in 3 cc. of N/10 acid. Titrate the excess of acid with N/50 alkali, using haematoxylin as indicator. Multiply the number of cc. of acid consumed, by the alkaloid, by 0.645 to obtain the percentage of alkaloid in the aconite.

The end reaction is usually green, but sometimes it is violet. In either case the end reaction is sharp.

Suitable modifications of this method are given or the assay of the tincture, fluid extract, and solid extract, and under the process for solid extract he remarks that it is: "Reliable for a properly made extract, but worthless for one that has been overheated."

Stevens' conclusions are as follows:

"1. That the decomposition products of aconitine, obtained by heat, are not the same as those formed by natural decomposition, as the former neutralize acid while the latter do not.

"2. That the lethal frog dose is not suited to the standardization of aconite.

"3. That Squibb's test is reliable for the purpose of determining the quality of aconite or its preparations, but that it is not as valuable for standardization as the chemical assay.

"4. That the chemical method is not reliable for the assay of extract.

"5. That the chemical method of assay is reliable when applied to the assay of aconite root, or its preparations, provided that they have not been subjected to heat."

As regards the unsatisfactory results from the lethal frog dose, he is probably correct, and in fact previous experiments arrive at the same conclusion (see page 556).

Stevens' third postulate is, I think, open to further consideration: If "the Squibb test is reliable for the purpose of determining the quality of aconite and its preparations," its entire suitableness as an assay is dependent solely upon its yielding sufficiently accurate or quantitative results for practical purposes or *under practical conditions such as confront the manufacturer, pharmacist and physician* who have to do with all the various derivatives of aconite; such products are of every possible variety, of different ages, manufactured under all sorts of conditions and of diverse strengths. Have we then in the chemical assay, a test to which must be added the proviso contained in the fifth conclusion quoted above, "——— provided they have not been subjected to heat?" How is one to know that such preparations have not been subjected to heat or other deleterious influences? If we take it for granted in any given case that this condition has been complied with, why not accept the preparation as of proper potency and avoid the bother of making any assay at all? The fourth conclusion would dismiss the solid and powdered extract of aconite altogether, but these are very generally sold and used, and justly esteemed as a concentrated aconite particularly well suited for use in pills and tablets, and we should be able to determine their strength. There is no difficulty in producing such an extract of full relative potency, providing the evaporation of the fluid extract be conducted *in vacuo* and at a low temperature. Contrasted with Stevens' experience as to the limited application of the chemical test, I have applied the Squibb test with much success indiscriminately to any and all derivatives of aconite, using 1 to 700 dilution for the fluid extract of the tuber as the standard, and adopting a proportionally higher or lower dilution for other preparations.

Lyons (68), after comparison of these two methods, arrives at the following conclusions:

1. The present official assay processes for aconite and its preparations should be discarded.

2. No chemical assay process of aconite and its preparations should be prescribed, which does not include identification of the alkaloid obtained as aconitine and insure the absence of inert alkaloids.

3. Official recognition should be given, at least provisionally to Doctor Squibb's test, as the only one by which at present the activity of aconite and its preparations can be practically judged.

Possible Source of Weakness in the Chemical Assay.—If Cash and Dunstan's conclusions (page 553) that benzoylaconine and aconine exert a greater or less inhibitive effect on aconitine are correct (and I believe they have not been controverted), then any chemical process which extracts all three together, or which estimates all the aconitine and a portion of the other two, or which estimates the aconitine alone while totally excluding the other two, is not to be recommended while there is available an assay like the Squibb test which indicates the power of the aconitine as modified by the secondary alkaloids present. In other words, the chemical assay, under these conditions, is not a true index to therapeutic value, whereas the Squibb test is such an index because it is based on physiologic reactions which undoubtedly form a part of the therapeutic action of the drug. This matter is further commented upon on page 564.

The Chemical Assay Compared with the Squibb Test.—It now remains to compare the results obtained by chemical assay and by the Squibb test. A series of assays by four chemical methods are given on page 556; from these it was decided to adopt the U. S. P. method, which is practically Stevens' method, as yielding the highest percentage of *aconitine*. A fluid extract was selected

and this was assayed gravimetrically, the alkaloid was also titrated with N/10 sulphuric acid, and fluid also tested by Squibb's method. A portion of the same fluid was then heated for two hours at 100° C. and assayed gravimetrically, by acid titration and by the Squibb test.

ASSAY BY METHOD IV, WITH AND WITHOUT PREVIOUS HEATING.

	Without previous heating	
	By weight.	By titration.
1	0.551	0.438
2	0.455	0.438
3	0.714	0.426
4	0.468	0.413
5	0.479	0.490
6	0.439	0.477
7	0.469	0.477
8	0.468	0.490
9	0.505	0.456

Responded to Squibb test in dilution of 1 : 700.

	Previously heated for 2 hours at 100° C.	
1	0.591	0.323
2	0.597	0.387
3	0.529	0.277
4	0.558	0.277
5	0.506	0.252
6	0.576	0.252
7	0.517	0.294
8	0.530	....
9	0.611	.....
10	0.664	....
11	0.575	.....

By Squibb test gave no reaction in dilution of 1 : 80.

In the assays upon unheated fluid, Nos. 1 and 3 by weight are high, especially the latter though their titration results are fairly concordant with 2 and 4. In numbers 5 to 8 the results by titration present the anomalous aspect of indicating more aconitine than can possibly be present. In the heated fluid the gravimetric assays show a markedly greater amount of aconitine present than before heating, and, though the results of the titration tend to correct the false indications of the gravimetric assays, yet they also are false for they show that after heating 64 per cent. of the aconitine remains, whereas the fluid fails to respond to the Squibb test in a dilution of 1:80, which proves that less than 12 per cent. of the original activity has survived the heating.

A solid extract was now made from the fluid on hand by very careful evaporation *in vacuo* at a temperature never exceeding 45° and most of the time under 40°. 200 cc. or practically 200 grams (sp. gr. being 1.009) were evaporated to an extract weighing 63 grams. This should test by calculation not less than 1:2222 by the Squibb test and in reality gave a good test at 1:2250, showing that none of the aconitine was injured. An assay on this in a manner similar to that used on the fluid gave results as follows:

	By weight Per cent.	By titration. Per cent.
1	2.77	1.03
2	2.73	0.99

Another sample of the same solid extract was heated for two hours at 100° and then tested both by assay and the Squibb test. The Squibb test showed a strength of 1:150, a loss in available aconitine of 93.3 per cent., in other words, a strength but 6.7 per cent. of what it was originally. The gravimetric assays showed almost the whole of the aconitine still intact; and though, as in case of the fluid extract above reported, the titration tended to reduce the error, still the assays by this method are very discordant and greatly above the truth.

	Solid extracts heated 2 hours at 100°.	
	By weight. Per cent	By titration. Per cent.
a	2.7	1.2
b	2.37	0.77

A second and different drug was now taken and from it was made a second fluid extract which we will call No. 2. Assays as in the first case were carried out on the drug and fluid extract with the following results:

	Drug No. 2.	
	By weight.	By titration.
1	0.849	0.825
2	0.852	0.813
	Fluid extract No. 2.	
1	0.850	0.774
2	0.909	0.697
3	0.852	0.761
4	0.887	0.761
5	0.874	0.748

By Squibb test responded in dilution 1 : 900.

Comparison of these results with those given for fluid extract No. 1 above show that No. 1 by Squibb test was 1:700 and No. 2 was 1:900, but while the chemical assay of No. 2 also yielded higher results than in No. 1, the excess is not nearly proportionate to the greater activity as indicated by the Squibb test. This discrepancy will be treated later and, I think, can be satisfactorily shown to be due to the greater proportion of secondary alkaloids in No. 1 drug (and fluid extract) which, while posing in the chemical assay as aconitine, are shown up in their true colors by the Squibb test as inhibiting the activity of the aconitine.

The Alkaloid from the Assay.—It now became desirable to examine more carefully the residue weighed and titrated as aconitine, and, inasmuch as the amount obtained from one or two assays

was too small, 500 cc. of fluid extract No. 1 were treated in exactly the same manner as an assay of 10 cc., using proportionately larger quantities of solvents and other reagents. The final ethereal solution was evaporated spontaneously in a warm room and dried *in vacuo* over sulphuric acid. The alkaloidal residue was a hard, brittle varnish, brownish in color, and crystallized in some places; its powder was brownish yellow. The amorphous varnish and the imperfectly crystalline spots were separated and the melting points of these differently appearing alkaloids determined. For both the crystalline part and that which was amorphous the melting point was 164–5°. At this temperature complete fusion occurred, but at about 83° a slight softening was noticeable which was more decided in the wholly amorphous part, but in neither case did it materially increase until very near the point of final melting.

The Squibb test on the total alkaloids showed 1 : 400,000.

The physical appearance and melting point showing the impurity of the recovered alkaloid, an attempt was made to separate the various alkaloids present by means of gold chloride. Dunstan and Jowett (12) have given the characteristics of aconitine-gold chloride at some length and Dunstan and Ince (2) have used gold chloride to determine the purity of aconitine. A small quantity of the crude alkaloid from fluid No. 1 was dissolved in N/10 hydrochloric acid and fractionally precipitated by adding successive small and equal quantities of gold chloride. A small part of the crude alkaloid was insoluble in the acid, proving the presence of a marked quantity of non-alkaloidal substance which was soluble in ether. This residue was largely fatty matter. Five portions of gold chloride were now added at intervals and the precipitate produced by each filtered off and tested.

Precipitate No. 1 was very small, pale yellow in color, amorphous and not entirely soluble in alcohol. The alcoholic solution when evaporated *in vacuo* gave no crystals, nor did a solution in acetone of this precipitate produce crystals when evaporated. The dry precipitate showed no definite melting point, softening at about 115° and melting fully about 125°.

Precipitate No. 2 was also very small and otherwise like No. 1 except in being entirely soluble in alcohol. Neither the alcohol nor acetone solution yielded crystals on evaporation *in vacuo*. The melting was similar to that of No. 1 in lack of definiteness, noticeable softening occurring about 110° and full fusion between 120° and 125°.

Precipitate No. 3 possessed the same characteristics as No. 2, both in quantity and other respects, with the exception of a slight difference in melting point. It softened first at about 115° and melted completely between 125° and 130°.

Precipitate No. 4 was very voluminous and flocculent, being by far the greater portion of the alkaloids. It was readily soluble in alcohol or acetone, a slight decomposition with separation of gold occurring with some readiness, which decomposition was probably caused by light. The melting point was quite different from that of the preceding fractions. It began to soften slightly at about 125°, but did not melt definitely until between 135° and 140°. This amorphous salt was thus evidently not entirely pure but the melting of the amorphous aconitine-gold chloride is given by Dunstan and Jowett (12) as about 137°, the exact point being indefinite, which corresponds well with the melting point found. The much lower points of fusion of the three preceding precipitates evidence their origin from a different base than aconitine.

Precipitate No. 5 thrown down slowly in minute quantity on the addition of another portion of gold chloride was characterized in general as the four preceding, but its melting point could not be obtained so its identity as aconitine-gold chloride was left in doubt.

From these experiments it becomes apparent that the residue obtained by assay as aconitine consists of at least three parts: aconitine, another alkaloid or alkaloids soluble in ether and precipitable by gold chloride, but distinct from aconitine, and a non-alkaloidal substance soluble in ether and insoluble in dilute acid.

To form some idea of the effect of heat on the alkaloid, 0.0500 gram was titrated and showed by calculation 0.0426 gram of aconitine. This seemed quite reasonable, but upon heating a second quantity of 0.0500 gram at 100° for 2 hours, titration of it showed 0.0490 gram aconitine present. Further, 0.0500 gram which had been dried *in vacuo* over sulphuric acid, when heated as the preceding, lost 0.0027 gram in weight. The Squibb test on another similar quantity also heated dry for 2 hours at 100° showed 1 : 400,000, as did the original before heating, this proving that practically no destruction of aconitine occurred. Dunstan and Ince (2) have also

shown that dry aconitine is uninjured by long exposure to a temperature of 100° and scarcely at all at 120°. The evidence therefore admits of but one conclusion; *viz.*, that the accompanying alkaloids or other foreign substances, and not the aconitine, are affected by the heat and that upon decomposition they yield some alkaline-reacting body which may pose as aconitine if titrated.

This resisting power of aconitine to heat suggested that in evaporating the ethereal solution obtained in the final step of the assay, such extreme care to avoid heat, as is usually considered necessary, is in reality not essential. To test this a small amount of aconitine was dissolved in ether saturated with water, producing a solution such as would be obtained from an assay. The ether was evaporated under a warm air blast having a temperature of 65° and the residual water evaporated in an air-bath at 100°, the crude aconitine being dried at this temperature for 2 hours. This severe treatment affected the aconitine but very slightly, as it still gave a Squibb test at 1:400,000, though very faint, not full and distinct as originally. It thus appears that, while aconitine is decomposed with extreme ease when heated in such preparations as the fluid or solid extract, in a fairly pure state it is less easily affected, though even yet by no means stable.

For the purpose of proving that all the aconitine was extracted by ether, a quantity of fluid extract No. 1 which had been treated according to Assay IV was subsequently extracted with chloroform. From the chloroformic solution a brownish varnish was obtained which was gummy and not easily powdered. This was an alkaloidal substance which melted uncertainly about 85°, was bitter to the taste and produced no tingling sensation on the tongue, showing the complete absence of aconitine. It seemed probable that this was impure aconine, but this question was not further dealt with, as the desired proof had been obtained, that all aconitine is extracted by ether.

Proof having thus been obtained of the impure and composite character of the alkaloid from fluid extract No. 1, 500 cc. of fluid No. 2 were extracted by the same assay method and the ethereal solution was allowed to evaporate spontaneously at room temperature. The residual alkaloid showed a marked tendency to crystallize, but was much contaminated with foreign matter. The residue was dried carefully for 48 hours in dry air at a temperature of 40° to 45°, and then weighed. From 500 cc., 4.222 grams crude alkaloid were obtained or 0.844 per cent., which corresponds to the assays of the same fluid, showing that the alkaloid extracted from the larger quantity of fluid was identical with that from 10 cc., so that an examination of it will give a true idea of the composition of the assay residue.

This alkaloid gave a Squibb test of 1:250,000. The crude alkaloid was dissolved as far as possible in 1 per cent. sulphuric acid with the aid of ether, evaporating all the ether finally under a blast of cold, dry air. A considerable quantity of the residue was insoluble in the acid solution and this was filtered off and washed, dissolved in ether, the solution transferred to a tared flask, dried carefully by spontaneous evaporation and then in a vacuum desiccator and finally weighed. A dark reddish brown residue of a composite character was obtained, which weighed 1.176 grams or 27.8 per cent. of the total alkaloid extracted by ether. This residue contained fat, resinous matter and apparently a quantity of amorphous alkaloid. The Squibb test showed a strength of aconitine remaining in this residue of 1:1500 or at the very largest estimate less than 1 per cent. of the total alkaloid.

The acid solution, consisting of filtrate and washings, was made alkaline with ammonia and extracted with ether. The ethereal solution being evaporated spontaneously in dry air yielded a mass of almost colorless crystals which were coated by a thin, slightly colored, amorphous varnish. This residue, dried with the usual precaution, weighed 1.981 grams. It pulverized readily, forming a cream-white powder, tested 1:600,000 by the Squibb test and melted at 175°. In determining the melting point a slight softening was observable at about 115°, due most probably to the trace of amorphous alkaloid accompanying.

Allowing the largest estimate of 1 per cent. aconitine present in the acid insoluble portion above, we will have 1.164 grams of this inert residue and 1.993 grams of almost pure aconitine. This leaves unaccounted for a quantity of matter remaining in the aqueous solution, which is soluble in ether and the acid water, but is not aconitine. We thus have separated the crude alkaloid into three distinct parts, and these are shown below in tabular form, with the weight from 500 cc., the percentage of the fluid extract and of the alkaloidal residue of assay.

Substance.	Weight from 500 cc. F. E. Grams.	Percentage of F. E.	Percentage of crude alkaloid.
Crude alkaloid	4.222	0.844	....
Purified alkaloid	1.993	0.398	47.2
Residue insoluble in 1% H_2SO_4	1.164	0.233	27.6
Substance soluble in 1% H_2SO_4 but not aconitine	1.065	0.213	25.2

The alkaloidal residue obtained in this case by the ether extraction assay, therefore, contains in reality but 47.2 per cent. of nearly pure aconitine which is evidence sufficient as to what value may be attached to the assay. Additional evidence to the same end is afforded by the difference between fluid extracts No. 1 and No. 2. Attention has been called to the discrepancy between them, and now the probable explanation appears.

	Squibb test on fluid.	Per cent. unpurified alkaloid (average).	Squibb test on unpurified alkaloid.
Fluid extract No. 1	1 : 700	0.47	1 : 400,000
Fluid extract No. 2	1 : 900	0.85	1 : 250,000

The Squibb test shows No. 2 fluid extract to be nearly 29 per cent. stronger than No. 1, while the weight of alkaloid indicates over 80 per cent. greater strength. The alkaloids resulting from the assay are much different by the Squibb test, that from No. 2 being 37.5 per cent. weaker than No. 1. It follows that, when the same method, worked in exactly the same manner on two well-made fluid extracts, gives such divergent results, there is good reason for believing that this chemical assay method is not reliable even for comparison only. These results are additional proof of the accuracy of the Squibb test. If a fluid which tests 1 : 700 gives on assay 0.47 per cent. of alkaloid testing 1 : 400,000, a second fluid testing 1 : 900 should give only 0.60 per cent. of alkaloid of like strength, or if it gives 0.85 per cent. the alkaloid so obtained should theoretically test 1 : 280,000. Again, this 0.85 per cent. impure alkaloid yields practically 0.4 per cent. of almost pure aconitine and this should test 1 : 530,000, while the observed test is 1 : 600,000, which does not agree so well.

The Squibb Test on the Fluid Compared to the Alkaloid.—This variation from theory is not without a cause and in seeking for it we find the following: Calculating from the basis of an alkaloid testing 1 : 400,000, a second alkaloid which should test 1 : 280,000 we find really tests 1 : 250,000 and notice that it is less pure than the first. A third which apparently should test 1 : 530,000 in point of fact tests 1 : 600,000 and is markedly purer than the first. Going back now to the original fluid extracts, we find that No. 1 which tests 1 : 700 yields 0.47 per cent. alkaloid which, calculating from this basis, should test 1 : 150,000, but actually tests 1 : 400,000, while No. 2 fluid extract testing 1 : 900 gives 0.85 per cent. of alkaloid theoretically of 1 : 106,000 strength and actually testing 1 : 250,000. This alkaloid purified produces 0.4 per cent. of alkaloid testing 1 : 600,000, which by calculation from the fluid should be 1 : 225,000. It will be noted that in the case of the three alkaloids compared the one least pure tested lower than theory based on the one of medium purity, while the one most pure tested much higher in proportion, or in other words, the greater the degree of purity of the alkaloid, the higher the test by the Squibb method. It appears that the obvious conclusion to be drawn is that bodies other than aconitine, present in the drug, its extracts and the impure alkaloid extracted by the chemical assay exert a decided influence on the Squibb test. These impurities are fatty and resinous matter, and amorphous alkaloids or basic bodies. It has been shown that there are normally present in the drug and consequently in the fluid extracts both benzoylaconine and aconine, and also that both these exert an inhibiting effect on aconitine; consequently they alter the therapeutic activity of aconitine wherever they may be associated with it. These alkaloids are not all extracted by ether, we know, and are thus present in greater quantity in the fluid extract than in the crude alkaloid extracted by ether, and we must also keep in mind that the difference between theory and fact in the case of fluid compared to alkaloid is greater than that of alkaloid compared to alkaloid. Either the alkaloidal or non-alkaloidal foreign matter, or both together, produce this inhibiting effect upon the peculiar tingling sensation caused by aconitine, but as this is extremely characteristic of aconitine, it is reasonable to suppose that where this characteristic test is not perceptible, from whatever cause, neither will the desired therapeutic effect be obtained if the same preparation be used medicinally. We are thus led to the conclusion that *the Squibb test does not show total aconitine but instead the far more essential factor, available* aconitine; that is, the amount of aconitine present from which we may expect its own natural medicinal action.

We know that aconine and benzoylaconine have such an inhibitory effect and it is not improbable that certain resinous bodies of aconite may act similarly. Absolute proof of this can, however,

not be obtained until extended comparisons of the Squibb test with the action of preparations on animals have been made.

Whatever the results of such a comparison may show, there is no question that the Squibb test will rapidly, and with a considerable degree of accuracy, show the therapeutic value of the root, tincture, fluid extract and solid extract of aconite in values entirely comparable among themselves. Since in all these the proportion of aconitine to antagonistic substance will remain nearly the same, such results necessarily follow. Whether or not further work shows that aconitine and other aconite preparations can be accurately compared in this manner except in an empirical way, the test is nevertheless certain evidence of the purity of the alkaloid.

SUMMARY.

In summary the following conclusions may be set forth:

1. That the determination of total alkaloids is of no value.

2. That the ether extraction process is the best of the chemical methods.

3. That the product of the ether extraction assay is not aconitine alone or in some cases even in greater part.

4. That this assay does not give even comparative results on fluid extracts made from different drug with equal care and is hence of little value.

5. That the chemical assay will not show the destruction of aconitine in a preparation, by heat or other causes, and is of no value in such cases.

6. That the Squibb test renders the drug, tincture, fluid extract and solid extract comparable in therapeutic value and is equally efficient on any preparation however made or previously tested.

7. That the Squibb test is both rapid and superior in accuracy to the chemical assay.

8. That the Squibb test is a certain criterion of the purity of aconitine.

9. That the Squibb test most probably indicates *available* aconitine.

10. That the Squibb test is simple enough to admit of its application by any pharmacist or physician.

11. And from the above, the general conclusion that in all the essential features of the assay as we have previously defined them, the Squibb test is more rapid, reliable and accurate than any other method so far proposed for the standardization of the root and preparations of aconite.

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LABORATORIES OF PARKE, DAVIS & CO.

THE USE OF TEMPERATURE CORRECTIONS IN THE POLARIZATION OF RAW SUGARS AND OTHER PRODUCTS UPON QUARTZ WEDGE SACCHARIMETERS.[1]

By C. A. BROWNE.

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I. INTRODUCTION.

Numerous papers have been presented at past meetings of the International Congress of Applied Chemistry upon "The Influence of Temperature upon the Specific Rotation of Cane Sugar." At the third meeting of the International Congress held in Vienna in 1898 Wiley[2] first read a paper upon "The Influence of Temperature on the Specific Rotation of Sucrose and Method of Correcting Readings of Compensating Polariscopes Therefor." In this paper it was demonstrated by numerous experiments that for each degree C. increase in temperature the polarization of pure cane sugar on quartz wedge saccharimeters decreased 0.03° Ventzke Wiley accordingly advocated that the readings of all quartz-wedge compensating polariscopes made at temperatures other than standard be corrected by means of this factor, and constructed a table of temperature corrections for polarizations between 75° V. and 100° V. for temperatures between 4° C. and 40° C., these corrections to be subtracted from the observed polarizations when the temperature of observation is below and to be added when the temperature is above that at which the instrument was standardized.

At the fourth meeting of the International Congress of Applied Chemistry, held in Paris in 1900, Wiley[1] presented another paper upon "The Corrections of Polariscope Readings for Changes in Temperature" in which he showed the magnitude of the variations produced in polarizations with different types of saccharimeters and the corrections necessary to restore the correct reading.

At this same meeting of the Paris Congress Wiechmann[2] presented a paper upon the "Question of Temperature Influence on the Specific Rotation of Sucrose" in which he opposed the views of Wiley. Wiechmann in his paper reviewed most critically the results of all previous investigations upon the subject and cited numerous experiments of his own upon the polarization of pure sucrose solutions, from which he concluded that chemically pure sucrose does not change its specific rotatory power with change in temperature and that no corrections should be made therefor in technical sugar analysis.

At the same meeting of the fourth International Congress a third paper upon "The Influence of Temperature on the Specific Rotation of Sucrose" was read by Pellat[3] who found as a result of his investigations that there was a progressive decrease in the specific rotation of sucrose with increase in temperature, the mean coefficient of variation between 14° and 30° being 0.00016. If we add to this value of Pellat for the temperature coefficient of sucrose the temperature coefficient[4] 0.000148 for the quartz compensation and

[1] Read before Section V, Seventh International Congress of Applied Chemistry, London, May, 1909.

[2] *Proc. Third Inter. Cong. App. Chem.*, Vol. II, p. 407, *J. Am. Chem. Soc.*, **21**, 568 (1899).

[1] *Proc. Fourth Inter. Cong. App. Chem.*, Vol. II, p. 142.

[2] *Ibid.*, Vol. II, p. 145.

[3] *Ibid.*, Vol. II, p. 135.

[4] Value determined by Schönrock, *Zeit Ver. Deut. Zucker Ind.*, **41**, tech. teil., p. 521.

scale we obtain the coefficient 0.000308, or for 100° Ventzke 0.0308, which is the same as the figure of Wiley.

The presentation of the papers of Wiley and Wiechmann at the Paris Congress, before the International Commission for Uniform Methods of Sugar Analysis, was followed by a long discussion, as a result of which it was generally agreed that, while the adoption of temperature corrections was not deemed advisable, sugar solutions should be made up to volume and polarized at a standard temperature of 20° in order to remove all influences of error.

The International Commission also passed the resolution that for countries whose temperature is higher than 20° saccharimeters may be adjusted at 30° or any other desired temperature providing that the analysis of sugar be made at the same temperature.

At the meeting of the fifth International Congress of Applied Chemistry held in Berlin in 1905, the question of the influence of temperature upon the specific rotation of sucrose was again discussed by Schönrock[1] in a paper entitled "The Dependence of the Temperature Coefficient of the Specific Rotation of Cane Sugar upon Temperature and Wave-length." Schönrock showed as a result of most careful physical measurements that the coefficient of the specific rotation of cane sugar was as follows:

$\partial^{D}_{10} = -0.000242$, $\partial^{D}_{20} = -0.000184$, $\partial^{D}_{30} = -0.000121$.

The value of ∂ decreases with increase of temperature.

For quartz wedge saccharimeters the above values for ∂ must be increased by 0.000148, the temperature coefficient for the quartz compensation and nickelin scale. The total correction calculated to 100° Ventzke is then 10° C. = 0.0390, 20° C. = 0.0332, 30° C. = 0.0269. The average factor between 20° C. and 30° C. is 0.0300 which is identical with the figure found by Wiley.

The influence of temperature upon the polarization of sucrose has, however, more than a theoretical interest. In the United States at least the question has been studied largely for the purpose of introducing greater accuracy in the polarization of raw sugars. The Treasury Department of the United States as a matter of fact incorporated in its Regulations of October 27, 1897, a method of correcting the influence of temperature upon the polarizations of all sugars imported into the United States and assessed for duty. The method of the Treasury Department consists in correcting the polarization of each sugar by the variation in reading which a standardized quartz plate will show from the computed sucrose value of this plate for the temperature of observation. Owing to the fact that the average daily temperature of most laboratories in the United States is above 20° this method of correction necessitates in almost every case an addition to the observed polariscopic reading.

The right of the U. S. Treasury Department to make any additions to the observed polarizations of sugars[1] was contested in the Courts by various importers of sugar, who held that any increase of temperature occurring in practice does not reduce the rotation of the sugar solution in the polariscope, nor does otherwise produce a lower test than that which would be obtained at any lower temperature occurring in actual practice, and that the assertion of some experts and the denial by others of the existence of any such alleged influence of temperature upon the rotatory power of sugar did not justify the Secretary of the Treasury in requiring additions to be made to the observed polariscopic test of imported sugars prescribed by law, and so increasing the rate of duty payable upon them above that prescribed by law. The importers in their petition furthermore contested the right of the Treasury Department to hold that the polariscopic test means "the percentage of pure sucrose contained in sugar as ascertained by polarimetric estimation."

The protest of the importers against the Treasury Regulations was overruled by the Board of General Appraisers in March, 1899. An appeal was accordingly taken to the Circuit Court which reversed, in May, 1903, the judgment of the General Appraisers, although expressing the opinion[2] that "despite the vehement protests and expert testimony on the part of plaintiffs to the contrary, the contention of the government"—(that there is a decrease in the reading of the polariscope with increase in temperature)—"is sustained by the preponderance of proof." In this reversal of the previous decision Judge Townsend of the Circuit Court made the following statement:[3] "The point has not been made on the argument, and it is perhaps irrelevant, but no reason is perceived why, if the government desires to secure uniformity and

[1] *Proc. Fifth Inter. Cong. App. Chem.*, Vol. III, p. 100.

[1] For particulars and testimony in this case see *Transcript of Record*, U. S. Supreme Court.

[2] *Federal Reporter*, **123**, 329 (Aug. 13, 1903).

[3] *Federal Reporter*, **123**, 330 (Aug. 13, 1903).

accuracy, it should not take its tests, or provide that they should be taken, at the temperature at which its instruments are standardized." This judgment of the Circuit Court was afterwards reversed in June, 1904, by the Court of Appeals[1] and the previous decision of the Board of General Appraisers sustained. The importers made a final appeal to the United States Supreme Court who dismissed the case on November 30, 1908, for want of jurisdiction.

The final decision of the Courts sustaining the Regulations of the U. S. Treasury Department in applying temperature corrections to the polarization of raw sugars settles the question no doubt once for all so far as Constitutional objections are concerned. But so far as scientific objections are concerned the case is far from settled. There are inherent difficulties in the application of temperature corrections to the polarization of raw sugars, molasses, massecuites, and other sugar house products. As a matter of fact when we cease to deal with pure sucrose the temperature correction employed by the Treasury Department in the assessment of sugar duties no longer corrects; in other words the corrected polariscope reading is not always the same as would be obtained upon this same product under the standard conditions of temperature. It is a matter of some surprise that in the case of the importers against the United States, which involved the correctness of the polarizations of raw sugars, no experiments showing the influence of temperature upon the optical rotation of raw sugars were presented. The experiments submitted as evidence of the correctness of the Treasury Department Regulations were all made upon pure sucrose.

The polariscopic test of a sugar, direct polarization, degree polarization, degree Ventzke, or whatsoever term it may be given, is a conventional expression representing the combined optical activities of the various ingredients present under certain prescribed conditions. The test cannot be construed to mean "the percentage of pure sucrose contained in the sugar" as held by the Treasury Regulations (Sec. 79, 1897; Sec. 49, 1907) except in the case of pure sucrose or in the case of a very small class of raw sugars where the optical activity of the sucrose is not influenced by the impurities present. The polarization is made to be sure upon a scale standardized to read 100 when the sugar polarized is 100 per cent. pure sucrose, but the polarization of a raw sugar upon this scale no more indicates the actual percentage of sucrose than it does in the case of molasses, honey, commercial glucose, condensed milk, or any other of the numerous products which are examined by means of a saccharimeter. To apply temperature corrections established for pure sucrose to the polarization of all substances whatsoever that are examined upon a saccharimeter would of course be an absurdity; the temperature correction to be applied will vary according to the nature of the substance examined.

It is perhaps superfluous to point out the error of the Treasury Regulations in considering "the degree of the Ventzke scale . . . . . as indicating the correct percentage of sucrose." (Treasury Regulations, Oct. 27, 1897, Sec. 79.) A few analyses of some Louisiana sugar-house products made by the writer in 1905 may be quoted, however, in passing.

TABLE I.

(Showing difference between polarization and sucrose of sugar-cane products.)

Product.	Direct polarization 20° C. Degree V.	Sucrose by Clerget. Per cent.	Difference.	Invert sugar. Per cent
Sugar..........	93 70	94 50	0 80	3 62
"	89.50	90.70	1.20	4.60
"	82 60	85 60	3.00	8.82
"	74.70	78 40	3 70	12.74
"	72.40	76.30	3.90	11.92
Syrup..........	54.35	58.50	4.15	12.20
Massecuite......	60.90	64.60	3.70	13.72
"	58.35	62.25	3.75	14.50
Molasses	41 30	45 45	4.15	11.72
"	34.00	37.80	3.80	14.27
"	28.90	37.05	8.15	27.43
"	16 00	26.90	10.90	27.05

A more complete exhibit of the difference between the direct polarization and sucrose content of raw sugars is given in Tables IV and XI.

It will be noted that the polarizations of sugar-cane products are in all cases much smaller than the percentage of sucrose, this difference increasing with the percentage of invert sugar present. The specific rotation of invert sugar according to Landolt[1] using Gubbe's formula for a 10 per cent. solution is -24.21 at 5°, -20.02 at 20°, and -16.81 at 30°. Calling $+66.5$ the specific rotation of sucrose, it is seen that one part of invert sugar neutralizes the optical power of 0.364 part sucrose at 5°, 0.301 part sucrose at 20° and 0.253 part sucrose at 30°. The average of the results in the previous table shows that one part of invert sugar neutralizes the optical activity of 0.315 part sucrose,

[1] *Federal Reporter*, **131**, 833 (Oct. 13, 1904).

[1] "Das Optische Drehungsvermögen," 2nd Edit., p. 526.

the individual figures varying above or below this according to the preponderance of dextrose or levulose in the mixture of the two sugars.

It is therefore evident that the polarization of a raw sugar or other product cannot be construed to mean the percentage of sucrose, but can only be taken as an expression of the sum of the optical activities of the various constituents, sucrose, dextrose, levulose, organic acids, gums, etc., which are present. It is furthermore evident that any system of temperature corrections, which shall give the polariscope reading that would be obtained upon a given product under standard conditions, must correct for the variations produced by temperature in the specific rotation of all the optically active ingredients therein contained. To correct for the sucrose alone, as by the Wiley table of corrections or by the sucrose values of quartz plates according to the Treasury Regulations, is accurate only in case of pure sucrose or in case the influence of temperature upon the specific rotation of the other constituents is so small as to be negligible. In all other cases the scheme of correction proposed will lead to erroneous results. That the influence of temperature upon the specific rotation of invert sugar is considerable has already been indicated; the extent of this influence in the polarization of raw sugars and other products will be considered in the experimental part of this paper.

The author has called attention to the above facts in numerous papers published in the past[1] and his more recent investigations have only more thoroughly convinced him of the futility of applying temperature corrections for the purpose of securing greater accuracy in general saccharimetric work.

II. Experimental Part.

The discussion of the numerous questions, which are involved in the investigation of raw sugars, will be much simplified if we regard such sugars as simple mixtures of pure sucrose crystals with varying amounts of molasses, either cane molasses or beet molasses as the case may be. This assumption is a perfectly valid one. The impurities of all raw sugars unless otherwise contaminated are the impurities of the mother liquors from which the sucrose is crystallized. The quantity of such mother liquor or molasses which remains adhering to the sugar crystals after purging in the centrifugals will vary in the case of cane sugar from the merest trace to over 30 per cent. The exact amount will depend upon many conditions, such as the purity of the syrup which is boiled to grain, the manner of boiling and crystallizing, the extent to which the sugar is washed in the centrifugals and other causes which need not be described. The coating of liquid molasses surrounding the individual grains of sucrose can be practically all removed by washing the sugar sufficiently in the centrifugals and perfectly white crystals are thus obtained. This process, known as affining, is always performed in the refinery preliminary to remelting; it is not, however, generally practiced upon the plantation in the manufacture of raw sugars.

The composition of the liquid coating of molasses surrounding the crystals of sucrose in raw sugars will also vary in composition according to the composition of the original syrup and the manner of boiling. A considerable amount of sucrose in a raw sugar exists in solution in the molasses. The skilful sugar boiler aims to keep this dissolved sucrose as low as possible and he does this by maintaining a low degree of supersaturation in the vacuum pan. A high degree of supersaturation in boiling will produce a thick molasses of relatively high purity; the excess of sucrose in such molasses does not crystallize out easily owing to the high viscosity of the solution and it remains dissolved in the raw sugar even after months of storage. The amount of such dissolved sucrose in raw cane sugars will vary from almost nothing to 12 per cent. or more. The ordinary polariscopic and chemical tests do not differentiate between the crystallized and dissolved sucrose. It is all estimated and valued alike, although of two sugars of equal polarization that containing the highest percentage of crystallized sucrose is necessarily of greatest value to the refiner.

The Influence of Temperature upon the Polarization of Different Solutions of Pure Sucrose.—In the present work the writer has accepted the value established by Wiley and other chemists for the variation in polarization of pure sucrose upon quartz compensating saccharimeters produced by changes in temperature, *viz.*, 0.03° Ventzke for each degree C. increase in temperature. The values for this constant reported by the different chemists who testified for the United States Government in the case brought by the importers for overcharge of duty, are as follows:

[1] *Louisiana Planter* **34**, 239. Proceedings of the Association of Official Agricultural Chemists, 1905 Meeting, *U. S. Bur. of Chem., Bull.* **99**, p. 20; 1908 Meeting, *Bur Chem., Bull.* **122**, p. 221.

Wiley.........	0.0314	(Given as testimony in the Transcript
Crampton......	0.0297	of Record Supreme Court of the United
Austin.........	0.0305	States. October Term, 1908. No. 3
Morton........	0.0298	The American Sugar Refining Com-
Tittman.......	0.0287	pany of New York, Appellant
Braid.........	0.0308	*vs.*
Huntington....	0.0307	The United States.)
Average.....	0.0302	

Of other values established for this constant may be mentioned.

0.030 Andrews (*Technology Quarterly*, May, 1889).
0.029 *The U. S. Coast and Geodetic Survey*.
0.030 Prinsen Geerligs (*Archief voor de Java Suikerindustrie*. July, 1903).
0.030 Francis (*Reports of Chem.*, British Guiana, 1883 and 1886).
0.031 Watts and Tempany (*West Indian Bull.*, Vol. VII, p. 140).

The values found by Schönrock and Pellat for this constant have been reported in the earlier part of this paper.

The above value has also been confirmed by the writer who found for the average decrease in polarization between 15° and 35° for each degree C. increase in temperature, the following results for 5 different sugar solutions:

TABLE II.

(Showing Influence of Temperature upon Polarization of Sucrose Solutions.)

Polarization of solution 20° C. 200 mm. tube. ° V.	Decrease in polarization for each 1° C. increase	Calculated decrease by formula 0.0003P.
100	0.031	0.030
90	0.026	0.027
70	0.019	0.021
50	0.014	0.015
20	0.002	0.006

The observed values agree closely with those calculated by the formula except in the case of the 20° V. solution where there may have been some slight experimental error. The writer, whose method will be described in the next section, performed his work upon weighed portions of the same solution (26 grams sucrose to 100 grams solution) so that accidental variations in the composition of the weighed sample are excluded. Whether the calculated correction for the temperature influence should be still further corrected for some slight variation through diminished concentration of the sucrose is an open question.

Methods of Preparing and Polarizing Solutions.—In order to eliminate all errors due to variations in sample, differences in volume of lead precipitate, and similar causes the polarization experiments upon raw sugars and other products were all performed upon the clarified solutions.

130 grams (5 times the normal weight 26 grams) of the sugar, molasses, etc., were dissolved in 370 cc. of cold distilled water. The solution was then clarified with a minimum quantity of anhydrous lead sub-acetate (Horne's preparation) and filtered. The slight excess of lead in the filtrate was then precipitated with the exact amount of potassium oxalate (avoiding excess) and the turbid solution filtered through kaolin. The first runnings of the filtrate which were usually somewhat milky, were discarded and only the clear bright after-portion used for polarization. In a few instances where lead did not decolorize sufficiently for accurate reading the solution was re-filtered through animal charcoal.

Two portions of 100 grams each of the clarified solution (26 grams approximately of substance) were weighed out into 100 cc. (metric) sugar flasks. One of the solutions was made up to volume and polarized in a room heated to 35° C.; the other solution was made up and polarized at about 12° C., the exact temperature depending upon the conditions of the outside weather.

The solutions were made up to volume and polarized in a small room 6 feet by 7 feet and 7 feet high, the temperature of which was raised from 20° C., that of the laboratory, to 35° by means of a small gas stove.

The saccharimeter upon which the observations were made was a late model Schmidt & Haensch double quartz wedge compensator, half shade, double field, and mounted upon trestle supports. The accuracy of the instrument had been thoroughly established before using by means of chemically pure sucrose and also by means of quartz plates standardized at the German Reichsanstalt and at the U. S. National Bureau of Standards. The quartz wedges and scale of the saccharimeter were enclosed in a case of sheet brass.

The temperature of the instrument was taken by means of three thermometers, one placed within the trough of the instrument with the bulb resting within the screw cap before the wedges, one placed at the side of the instrument with the bulb against the brass wall of the wedge encasement, and one placed in front of the instrument with its bulb inserted in one of the telescope tubes, the eyepiece of the latter having been temporarily removed.

When the three thermometers each indicated 35°, the temperature was controlled at this point for 1 to 1½ hours before beginning the observations, at the end of which time it was assumed that the quartz wedges had acquired the surrounding temperature.

The solutions in the flasks were made up to 100 cc. at the same temperature as the instrument and the

solutions polarized in 200 mm. tubes. The temperatures of the solutions in the flasks after making up the volume and in the observation tubes after polarizing were taken as additional checks.

The light used for polarizing was supplied by a 32-candle power stereopticon electric incandescent lamp and was filtered through a 3 per cent. solution of potassium bichromate in a 3 cm. cell.

The zero point of the instrument was determined before and after each series of observations and the average of the two sets of determinations used as the zero point correction for the series. The determination of the zero point was made by means of the control wedge at 10 different points of the scale, the average of the differences between the scale readings of the working and control wedges at these points being taken as the true zero. In determining the zero point a 200 mm. tube filled with distilled water was always placed in the trough of the instrument in order to secure as nearly as possible the same conditions as in the work of polarization.

In making the polarizations ten readings were taken at various positions of the working and control wedges, the difference between the readings being taken as the polarization. The average of the ten polarizations was then corrected for the zero point as above described and the final result taken as the true polarization of the solution at the temperature of the instrument.

The high temperature observations were made late in the afternoon and the low temperature observations early the next morning. The heat of the laboratory was turned off the previous evening and the windows slightly raised. For the low temperature work the temperature of saccharimeter and room according to weather conditions ranged from 8° to 15°. Zero point corrections, making up of solutions to volume and polarizations were made in the manner previously described.

The difference between the polarization at high and low temperature divided by the difference in temperature gives the variation in the reading of the saccharimeter for each degree C. change.

All flasks, tubes, weights, thermometers, etc. used in the experiments had been previously tested as to accuracy. The error of the 100 cc. flasks employed was less than 0.05 cc. and the error of the 200 mm. tubes less than 0.1 mm. No correction for the slight errors within these limits was introduced into the calculation, as they were smaller than could be measured by the saccharimeter, which could be read only to 0.05° V. Furthermore, the work was performed upon different products using different flasks and tubes and the conclusions arrived at based upon a general average so that slight errors due to variations in the capacity of the flask or length of tube or other cause would be largely eliminated. The differences observed in the readings made at different temperatures are simply such as would be noted in the routine work of commercial analysis.

Influence of Temperature upon the Polarization of Sugar Cane Molasses.—In the winter of 1905 the writer made a series of observations at the Louisiana Sugar Experiment Station upon the influence of temperature on the polarization of low-grade Louisiana molasses. The results of this work are given in the following table under Nos. 1, 2, and 3. Sample No. 4 is another product of Louisiana third molasses recently examined by the writer at The New York Sugar Trade Laboratory.

TABLE III.

(Influence of Temperature on the Polarization of Louisiana Molasses.)

Sample No	Polarization 20° C. Degree V.	Sucrose. Per cent.	Invert sugar. Per cent.	Ash. Per cent.	Water. Per cent	Gums, acids, nitrogenous substances, etc. Per cent.	Temperature factor change in polarization for 1° C. increase. Degree V.
1	21.05	31.25	27.53	10.55	20.02	10.65	+0.1075
2	16.00	26.89	29.85	9.13	23.06	11.07	+0.1122
3	20.55	28.08	32.61	6 49	26 46	6.36	+0.1172
4	22.65	32.10	30.38	6.80	24.94	5.72	+0.1113
Ave.	20.06	29.58	30 09	8.24	23 62	8.47	+0 112

The results show that for the average exhausted Louisiana molasses polarizing 20° V. and containing about 30 per cent. sucrose and 30 per cent. invert sugar, there is an increase in polarization of 0.112° V. with each degree C. increase in temperature. The effect of temperature upon the polarization of cane molasses is therefore nearly 4 times as great as that upon the polarization of pure sucrose and *in the opposite direction.*

The principal agent affecting the temperature changes in the polarization of cane molasses is not the sucrose, but as is well known, the levulose and this change is so pronounced that a method has been worked out by Wiley[1] for determining the percentage of levulose in sugar mixtures by measuring the difference in polarization at wide intervals of temperature.

The effect of temp rature upon the polarization

[1] "Principles and Practice of Agricultural Analysis." Vol 3 p 267

of levulose may be easily calculated from the formula of Jungfle sch and Grimbert $[\alpha]_D^t = -[101.38 - 0.56t + 0.108 \ (c - 10)]$. The specific rotation according to the above formula for the normal weight of pure levulose (c = 26 grams) at 5° C. would be —100.31° and at 30° C. —86.31. The equivalent in degrees of the Ventzke sugar scale for the normal weight of levulose at 5° C. would then be (—100.31 × 100) ÷ 66.72 ($[\alpha]_D^{5°}$ sucrose) = —150.4° V. and at 30° C. (—86.31 × 100) ÷ 66.36 ($[\alpha]_D^{30°}$ sucrose) = —130.1° V. The difference in reading of a normal weight of pure levulose (100 metric cc. 200 mm. tube) is therefore 20.3° V. toward the right for 25° C. or 0.812° V. for 1° C. increase in temperature.

The average exhausted cane molasses of 30 per cent. invert sugar content would contain approximately 15 per cent. of levulose. 15 per cent. of 0.812° V. is 0.1218° V., the deviation toward the right for 1° C. increase due to the levulose of the molasses; subtracting from this the deviation toward the left for 1° C. increase due to the 30 per cent. sucrose of the molasses (30 per cent. of 0.03 = 0.009) we obtained the difference +0.1128, which agrees almost exactly with the average change in polarization for 1° C. increase that was obtained experimentally.

Determination of the Influence of Temperature upon the Polarization of Raw Cane-Sugars.—It is now possible to calculate the influence of temperature upon any mixture of sucrose crystals and cane molasses. Adding together the polarizations and percentages of the ingredients in the sucrose and molasses taken will give the polarization and percentage composition of the resulting raw sugar, and similarly adding together the respective influences of temperature upon the polarization of the sucrose and molasses will show the influence of temperature upon the corresponding raw sugar.

A molasses of 20.00° V. polarization, 30 per cent. sucrose, 30 per cent. invert sugar, and +0.112 temperature factor was taken as a basis in the following table. The method of computation may be illustrated by the following example:

	Polarization.		Sucrose.		Invert sugar.		Temperature factor.
Sucrose (80% of 100)	80.00		80.00		0.00	(80 × —0 00030)	—0 0240
Molasses (20% of 20)	4.00	(20% of 30)	6 00	(20% of 30)	6.00	(20 × +0.00112)	+0 0224
Raw sugar.........	84.00		86.00		6.00		−0.0016

In the same manner as the above the calculations of Table IV were made upon 25 mixtures of sucrose crystals and molasses; the percentages of added molasses ranged from 0.0 to 30 per cent. and the polarizations of the mixture from 76 to 100.

TABLE IV.

(Showing Influence of Temperature upon the Polarization of Calculated Mixtures of Sucrose Crystals and Exhausted Louisiana Molasses)

Per cent. sucrose crystals.	Per cent. molasses.	Polarization.	Sucrose. Per cent.	Invert sugar. Per cent.	Temperature factor. Actual.	Temperature factor. By formula 0.0003P.
100.00	0.00	100.00	100.00	0.00	—0.0300	—0 0300
98.75	1.25	99.00	99.12	0.38	—0.0282	—0.0297
97.50	2.50	98.00	98.25	0.75	—0.0265	—0.0294
96.25	3.75	97.00	97.37	1.13	—0.0247	—0.0291
95.00	5.00	96.00	96.50	1.50	—0.0229	—0.0288
93.75	6.25	95.00	95.62	1.88	—0.0212	—0.0285
92.50	7.50	94.00	94.75	2.25	—0.0194	—0.0282
91.25	8.75	93.00	93.87	2.63	—0.0176	—0.0279
90.00	10.00	92.00	93.00	3.00	—0.0158	—0.0276
88.75	11.25	91.00	92.12	3.38	—0.0141	—0.0273
87.50	12.50	90.00	91.25	3.75	—0.0123	—0.0270
86.25	13.75	89.00	90.37	4.13	—0.0105	—0.0267
85.00	15.00	88.00	89 50	4 50	—0 0087	—0.0264
83.75	16.25	87.00	88.62	4.88	—0.0070	—0.0261
82.50	17.50	86.00	87.75	5.25	—0.0052	—0.0258
81.25	18.75	85.00	86.87	5.63	—0.0034	—0.0255
80.00	20.00	84.00	86.00	6.00	—0.0016	—0.0252
78.75	21.25	83.00	85.12	6.38	+0.0002	—0.0249
77.50	22.50	82.00	84.25	6.75	+0.0020	—0.0246
76.25	23.75	81.00	83.37	7.13	+0.0038	—0.0243
75.00	25.00	80.00	82.50	7.50	+0.0055	—0.0240
73.75	26.25	79.00	81.62	7.77	+0.0073	—0.0237
72.50	27.50	78.00	80.75	8.25	+0.0091	—0.0234
71.25	28.75	77.00	79.87	8.63	+0.0108	—0.0231
70.00	30.00	76.00	79.00	9.00	+0.0126	—0.0228

The temperature factors of the above table can be verified by making the calculations upon the percentage of levulose, in the manner previously described. Example:

For an 84 test sugar of the table there would be the following:

Temperature factor for 86% sucrose (86 × —0 0003)	= —0.0258
" " " 3% levulose (3 × +0.00812)	= +0.0244
" " " 84 test sugar	= —0.0014

which is in very close agreement with the result of the table —0.0016.

It will be noted from the results of the above table that for very high-grade sugars the temperature factor calculated for the mixtures of sugar crystals and molasses and that calculated by the formula 0.0003P are in very close agreement. The percentage of levulose in the raw sugar is too small to affect appreciably the temperature factor of the sucrose. As the polarization falls below 96–97 and the percentage of levulose increases, the effect of the temperature upon the rotation of the latter begins to lower appreciably the sucrose factor until

at a point about 83° V. the two influences—that of the temperature upon the levulose and other impurities and that of the temperature upon the sucrose and quartz wedges of the instrument—exactly counterbalance one another. Two chemists polarizing such a sugar, one working at 30° C. and one working at 20° C., other conditions being equal, would obtain perfectly concordant and correct readings; the application of the theoretical sucrose correction would place the observation of the chemist working at 30° C. 0.25° V. too high.

Below 83° the effect of temperature is seen to increase rather than diminish the reading. The levulose correction more than counterbalances the sucrose factor. Every chemist knows how pronounced this influence of temperature upon the levulose is in the polarizations of syrups and molasses, how the simple handling of the observation tubes will increase the reading. The same influence is manifested with low-grade cane-sugars only to a less degree. When such sugars are polarized above 20° C. a correction would have to be subtracted to secure the reading that would be obtained under standard conditions. To add a correction, as required by the U. S. Treasury Department Regulations, would manifestly only further increase the errors of observation.

The results of Table IV were calculated for mixtures of sucrose crystals and Louisiana molasses. Variations in the composition of the molasses, according to locality and methods of manufacture, will necessarily affect the temperature factor of the sugar. The results upon many grades of commercial sugars from different countries given in the succeeding tables agree, however, on the whole very closely with those calculated upon the basis of Louisiana molasses.

In the following table polarizations and analyses are given of various commercial sugars testing over 96. The temperature factor (change in polarization for 1° C. increase in temperature) of each sugar in this and succeeding tables was determined by the method previous'y described. The temperature factor as calculated from the polarization (P) by the expression 0.0003P, is also added for purpose of comparison.

The temperature factor observed for such sugars as polarize over 96 is seen to agree very closely with that calculated from the formula and the application of the latter as a correction in the polarization of such grades of raw sugar would unquestionably increase the accuracy of the observation.

TABLE V.

(Showing Influence of Temperature upon the Polarization of Commercial Sugars Testing over 96° V.)

						Temperature factor (change per 1° C. increase).	
No.	Source of sugar.	Polarization 20° C. Degree V.	Invert sugar. Per cent.	Moisture. Per cent.	Ash. Per cent	Found. Degree V.	By formula 0.0003P. Degree V.
1	Java	98.55	0.64	0.19	0.21	—0.0311	—0.0296
2	"	97.85	0.82	0.23	0.52	—0.0268	—0.0294
3	Peru	97.95	1.29	0.43	0.29	—0.0315	—0.0294
4	"	97.45	0.52	0.45	0.46	—0.0301	—0.0292
5	Cuba..........	97.15	0.78	1.03	0.31	—0.0276	—0.0291
6	Brazil..........	96.55	1.98	0.64	0.25	—0.0291	—0.0290
7	Louisiana......	96.40	1 99	0.93	0.70	—0.0277	—0.0289
8	San Domingo ..	96.25	1.02	1.54	0.77	—0 0313	—0.0289
9	" " ..	96.15	1 53	0.85	0.48	—0.0230	—0.0288
	Average	97.14	1.17	0.70	0 44	—0.0287	—0.0291

The average temperature factor of —0.0287 is a little higher than that calculated for a 97 test sugar in Table IV, *viz.*, —0 0247. The difference can be attributed to the diminished ratio of levulose to dextrose in the reducing sugars of the juice of more matured cane of tropical countries as compared with that of Louisiana molasses.

In Table VI polarizations, analyses and temperature factors are given for various commercial sugars testing between 90 and 95.

TABLE VI.

(Showing Influence of Temperature upon the Polarization of Commercial Sugars Testing between 90 and 95° V.)

						Temperature factor (change per 1° C. increase).	
No.	Source of sugar.	Polarization 20° C. Degree V.	Invert sugar Per cent.	Moisture Per cent.	Ash Per cent.	Found. Degree V	By formula 0 0003P. Degree V.
10	Cuba	94 50	1.83	1.97	0 63	—0 0212	—0.0287
11	"	93 75	2 29	1 83	0.55	—0 0160	—0.0281
12	"	92.57	3 36	1.32	0 43	—0.0077	—0.0278
13	Louisiana	92 30	2.68	1.11	2 65	—0.0240	—0.0277
14	Cuba.........	91.75	2.12	2.00	3.28	—0.0244	—0.0275
15	Philippines ..	91 45	3 97	2.11	1.27	—0.0074	—0.0274
	Average	92.72	2.71	1 72	1.47	—0.0168	—0.0278

The temperature factor for the sugars in the above table is seen to be very variable; where the percentage of invert sugar is high as in Nos. 12 and 15 the temperature factor is much lower than in sugars of equal polarization, but lower invert sugar content. The temperature factor calculated by the formula 0.0003P is very much too high. The average of the results for invert sugar and temperature factor for the sugars in Table VI agrees

almost exactly with that calculated for 92.7 test sugar in Table IV.

In Table VII results are reported upon ten sugars testing between 85 and 90.

TABLE VII.

(Showing Influence of Temperature upon the Polarization of Commercial Sugars Testing between 85 and 90° V.)

No.	Source of sugar	Polarization. Degree V.	Invert sugar. Per cent.	Moisture. Per cent.	Ash. Per cent.	Temperature factor (change per 1° C. increase). Found. Degree V.	By formula 0.0003P. Degree V.
16	Cuba.........	89.50	2.05	3.54	1.13	—0.0139	—0.0269
17	Philippines ...	89.20	4.63	2.11	1.27	—0.0110	—0.0268
18	Brazil (Muscovado)..	88.90	4.46	5.40	0.86	—0.0023	—0.0267
19	West Indies ..	88.50	4.77	5.44	1.03	—0.0077	—0.0266
20	Louisiana	87.60	4.67	2.30	3.17	—0.0106	—0.0263
21	Cuba.........	87.20	4.24	3.55	4.93	—0.0094	—0.0262
22	Cuba.........	87.00	2.11	2.42	1.49	—0.0180	—0.0261
23	Brazil (Muscovado)...	86.80	4.46	5.61	1.15	—0.0143	—0.0260
24	S. American (Muscovado)..	86.70	4.81	4.65	1.49	—0.0156	—0.0260
25	Brazil (Muscovado)	86.15	4.46	5.19	1.25	—0.0162	—0.0258
	Average....	87.76	4.07	4.02	1.78	—0.0119	—0.0263

It will be noted that the temperature factor observed for raw cane-sugars polarizing between 86 and 90 is less than half that calculated by the formula. The average factor —0.0119 for an 87.76 test sugar is somewhat higher than that indicated by Table IV. The difference is explained by the fact that the sugars of Table VII average about 0.5 per cent. less invert sugar than the sugars of same polarization in Table IV. By calculating the temperature factor of the above average from the percentage of levulose, however, the same result is obtained. Letting the sucrose = P + 1/3 per cent. of invert sugar, the average per cent. of sucrose = 89.12.

Sucrose factor	= 89.12 × —0.0003	= —0.0267
Levulose "	= 2.04 × +0.00812	= +0.0166
Calculated temperature factor		= —0.0101
Observed " "		= —0.0119

In Table VIII results are reported upon 6 sugars testing between 80 and 85.

The temperature factor of the following sugars is seen to average only 1/5 that calculated by the polarization formula. The average factor —0.005 for a sugar testing 82.8 is slightly above that indicated by the table (+0.005). This difference as in the previous example is due to the lower content of invert sugar. By making the calculations from the sucrose and levulose percentages, in the manner described under Table VII, a temperature factor is found of —0.025 for the sucrose and +0.023 for the levulose and for the combined influence of the two —0.002 which is practically identical with the temperature factor found.

TABLE VIII.

(Showing Influence of Temperature upon the Polarization of Commercial Sugars Testing between 80 and 85° V.)

No.	Source of sugar.	Polarization 20° C. Degree V.	Invert sugar Per cent.	Moisture. Per cent.	Ash. Per cent.	Temperature factor (change per 1° C. increase). Found. Degree V.	By formula 0.0003P. Degree V.
26	Cuba..........	84.70	3.69	4.26	2.63	—0.0115	—0.0254
27	Philippine (Mats)......	84.10	7.38	3.49	1.85	—0.0021	—0.0252
28	Philippine (Mats)	82.55	7.31	3.49	1.85	—0.0031	—0.0248
29	Philippine (Mats)........	82.40	7.45	3.49	1.85	0.0000	—0.0247
30	Cuba..........	82.05	3.21	4.05	3.57	—0.0145	—0.0246
31	Cuba	81.00	5.45	4.85	2.77	—0.0039	—0.0243
	Average.....	82.80	5.75	3.94	2.42	—0.0051	—0.0248

It will be noted that for such sugars as the above the temperature factor is practically 0; for an average sugar of this class the same polarization would be obtained at 30° C. as at 20° C. The application of the correction 0.0003P would result in the addition of 0.25° V. to the polarization obtained at 30°.

In Table IX results are reported upon several sugars which tested less than 80° V.

TABLE IX.

(Showing Influence of Temperature upon the Polarization of Commercial Sugars Testing under 80° V.)

No.	Source of sugar.	Polarization 20° C. Degree V.	Invert sugar Per cent.	Moisture Per cent.	Ash. Per cent.	Temperature factor (change per 1° C. increase). Found. Degree V.	By formula 0.0003P Degree V.
32	Louisiana....	79.65	6.80	4.84	4.21	+0.0068	—0.0239
33	Cuba........	78.80	4.21	5.05	2.70	—0.0045	—0.0236
34	Cuba........	78.55	4.53	4.80	2.83	—0.0105	—0.0236
35	Cuba........	67.70	11.18	6.70	3.75	+0.0286	—0.0203
	Average....	76.18	6.68	5.35	3.37	+0.0051	—0.0228

The temperature factor of all low-grade cane-sugars will necessarily vary considerably, owing to fluctuations in percentages of invert sugar and moisture. The average factor for the four sugars in Table IX shows an increase in polarization of

0.005° V. for 1° C. increase for a sugar testing about 76. This varies a little from the value indicated in Table IV, but by making the calculations from the content of levulose and sucrose in the manner previously described we obtain a factor of +0.0270 for the levulose and —0.0235 for the sucrose and for the combined influence of the two a factor of +0.0035, which is in close agreement with the temperature factor found.

The temperature factor calculated by the formula 0.0003P shows a decrease of —0.0228 for each degree C. increase. In other words the polarization formula would add a correction of 0.23° V. to a cane-sugar testing 76 at 30° C., whereas in reality a correction of 0.05 should be subtracted from the reading in order to obtain the true polarization at 20° C.

It should be remarked in passing that the errors involved in the application of sucrose temperature corrections to the polarization of raw cane-sugars may be still further intensified if the correction is made by means of the U. S. Treasury Department table of sucrose values, when quartz plates are used which test higher than the sugar under examination. It is wrong in principle to apply the correction for a 100° V. quartz plate, for example, to a sucrose solution testing 50° V., yet the writer has known of chemists applying the correction for the sucrose value of 100° V. quartz plates to the polarization of raw sugars, syrups, molasses, and all other products which were examined upon the saccharimeter.

Conditions Underlying the Application of Temperature Corrections to the Polarization of Raw Cane-Sugars.—The errors involved in the application of the U. S. Treasury Department method of temperature corrections to the polarization of raw cane-sugars have an additional significance in view of the fact that the lowest grades of sugar arrive for the most part at the ports of the United States in the warmest months of the year when the correction errors would be the greatest. This can be seen best from an inspection of Table X which gives the monthly distribution by grade of the raw sugars analyzed at the New York Sugar Trade Laboratory for 1908. The results are expressed in percentages of the total number of samples analyzed for the year.

TABLE X.

DISTRIBUTION OF SUGARS BY GRADE FOR EACH MONTH OF 1908.

Polarized at The New York Sugar Trade Laboratory.

(In Percentage of Total Number for the Year.)

Polarization.	Jan. Per cent.	Feb. Per cent.	March. Per cent.	April. Per cent.	May. Per cent.	June. Per cent.	July. Per cent.	Aug. Per cent.	Sept. Per cent.	Oct. Per cent.	Nov. Per cent.	Dec. Per cent.	Total. Per cent.
97–100	0.37	0.59	0.15	0.38	0.37	0.15	0.75	0.64	3.28	5.55	4.41	2.75	19.39
96– 97	0.76	2.54	3.16	2.47	1.44	0.89	0.89	0.47	0.43	0.09	1.00	0.82	14.96
95– 96	1.00	5.22	5.96	6.64	3.47	2.35	1.49	0.99	0.73	0.36	0.58	0.55	29.34
94– 95	0.34	2.07	2.46	2.84	3.30	1.27	1.39	0.79	0.63	0.35	0.14	0.08	15.66
90– 94	0.62	0.47	0.72	0.60	1.87	1.29	1.47	0.58	0.30	0.89	0.21	0.13	9.10
85– 90	0.06	0.02	0.36	0.42	1.41	2.19	1.31	1.23	0.95	0.13	0.26	0.14	8.48
70– 85	0.03	0.02	0.03	0.20	0.33	0.27	0.46	0.84	0.45	0.11	0.33	0.00	3.07
Total.......	3.18	10.93	12.84	13.55	12.19	8.41	7.71	5.54	6.77	7.48	6.93	4.47	100.00
Mean polar ...	95.00	95.52	95.21	95.04	93.81	92.78	93.21	91.59	94.28	97.13	96.87	96.55	......
Mean temp. C°..	20.37	20.50	20.42	20.46	22.14	25.68	27.93	25.38	22.38	20.22	20.59	20.25	......
Max temp. C°..	21.5	21.0	21.0	22.0	27.0	29.0	31.0	30.0	24.50	22.0	21.5	21.5	......
Min. temp. C°..	18.5	20.0	20.0	19.0	20.0	23.0	26.0	20.0	20.0	18.0	19.0	19.5	......

Total samples analyzed for 1908, 9,215.

Average of all polarizations for 1908, 94.68.

It will be noted that the maxima of the highest grade sugars occur in the cool months and the maxima of the lowest grade in the warm months, there being a progressive lowering of the quality of sugar as the warm weather of summer advances.

The temperature of a laboratory in the climate of New York need rarely exceed 20° C. from October until May, and in this period of 7 months 60 per cent. of all the raw sugars polarized were received.

The remaining 40 per cent. of sugars arrived in the summer months when the average laboratory temperature exceeded considerably 20° C. and polarization under standard conditions is not possible without artificial refrigeration. The application of the formula $P^{20} = P^{t}[1 + 0.0003\,(t - 20)]$ would be approximately correct, as we have seen, with sugars polarizing over 96, which for the warm months make up about 9 per cent. of the total. The above formula would also hold partially for the large class of centrifugals polarizing between 95 and 96 which for the warm period make up also about 9 per cent. of the total. For the sugars testing under 95, over 22 per cent. of the year's total for the warm months, the formula gives a polariza-

tion considerably in excess of the true reading at 20°, the error amounting to over 0.3° V. on very warm days with low-grade Cuban and Philippine sugars. The same error would extend of course to sugars polarized in the cool months of the year in case of laboratories heated above 20° C.—the general condition in the United States.

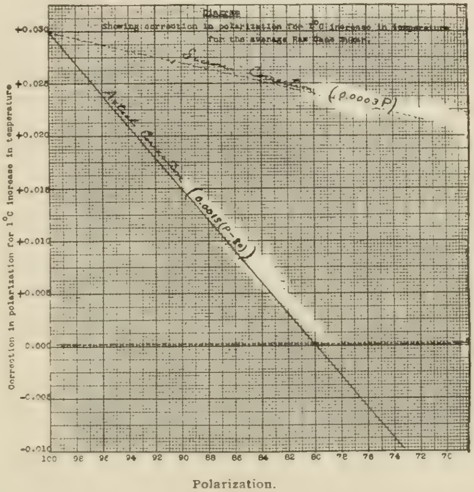
Table XI, which is based upon the average of the various results previously presented, gives the approximate composition of raw cane sugars and the change in the polarization of the same for each degree C. increase in temperature. The results agree closely with those of Table IV upon the theoretical mixtures of sucrose crystals and molasses; the small differences are due to the slightly lower content of invert sugar (and hence of levulose) in the average raw cane-sugar than in those calculated upon the basis of Louisiana molasses.

TABLE XI.

(Showing Approximate Composition of Raw Cane Sugars and Variation in Polarization for 1° C. Increase in Temperature.)

Polarization. Degree V.	Sucrose. Per cent.	Invert sugar. Per cent.	Ash. Per cent.	Moisture. Per cent.	Organic Non-sugar. Per cent.	Variation in polarization for 1° C. increase. Actual. Degree V.	By formula 0.0003P. Degree V.
100.00	100.00	0.00	0.00	0.00	0.00	—0 0300	—0 0300
99.00	99.10	0.35	0.15	0.25	0.15	—0 0285	—0.0297
98.00	98.20	0.70	0.30	0.50	0.30	—0.0270	—0.0294
97.00	97.30	1.05	0.45	0.75	0.45	—0 0255	—0 0291
96.00	96.40	1.40	0.60	1.00	0.60	—0 0240	- 0 0288
95.00	95.50	1.75	0.75	1.25	0.75	—0 0225	—0 0285
94.00	94.60	2.10	0.90	1.50	0.90	—0 0210	- 0 0282
93.00	93.70	2.45	1.05	1.75	1.05	—0.0195	—0.0279
92.00	92.80	2.80	1.20	2.00	1.20	—0 0180	—0 0276
91.00	91.90	3.15	1.35	2.25	1.35	—0.0165	—0 0273
90.00	91.00	3.50	1.50	2.50	1.50	—0.0150	—0 0270
89.00	90.10	3 85	1.65	2.75	1.65	—0 0135	—0.0267
88.00	89.20	4.20	1.80	3.00	1.80	—0.0120	—0 0264
87.00	88.30	4.55	1.95	3.25	1.95	—0 0105	—0 0261
86.00	87.40	4.90	2.10	3.50	2.10	—0 0090	—0.0258
85.00	86.50	5.25	2.25	3.75	2.25	—0 0075	—0.0255
84.00	85.60	5.60	2.40	4.00	2.40	—0.0060	—0 0252
83.00	84.70	5.95	2 55	4 25	2 55	—0.0045	—0 0249
82.00	83.80	6.30	2.70	4.50	2.70	—0.0030	—0 0246
81.00	82.90	6.65	2.85	4.75	2.85	—0 0015	—0.0243
80.00	82.00	7.00	3.00	5.00	3.00	0.0000	—0.0240
79.00	81.10	7.35	3.15	5.25	3.15	+0.0015	—0 0237
78.00	80.20	7.70	3.30	5.50	3.30	+0.0030	—0.0234
77.00	79.30	8.05	3.45	5.75	3.45	+0 0045	—0.0231
76.00	78.40	8.40	3.60	6.00	3 60	+0.0060	—0.0228
75.00	75.50	8.75	3.75	6.25	3.75	+0.0075	—0.0225

The approximate corrections necessary to be applied to the polarization of raw cane-sugars for 1° C. increase are of course obtained by simply reversing the algebraic signs of the values in Table XI. The following general formula for correcting the polarization (P) at $t°$ of any raw cane-sugar to $P^{20°}$ is calculated from the values of Table XI; $P^{20} = P^t + 0.0015\ (P^t - 80)\ (t° - 20)$. The correction in polarization for 1° C. increase in temperature for the average raw cane-sugar is also shown graphically in the diagram. The correction by the formula 0.0003P is also given for comparison.



The Effect of Temperature upon the Polarization of Beet Products.—In connection with the results obtained upon sugar-cane products it was thought well to make a few comparisons regarding the effect of temperature upon the polarization of similar materials derived from the sugar beet. The latter differ in composition in several important respects from products of the sugar-cane. In distinction from the latter beet molasses and raw beet sugar contain but small amounts of reducing sugars and a much higher percentage of nitrogenous substances. Beet products are also usually characterized by the presence of the sugar raffinose in small amount. The polarization of beet products agrees more closely with the true sucrose content than is the case with cane products. The application of the temperature correction for sucrose to the polarization of raw beet sugars would therefore seem upon theoretical grounds less open to objection than with raw cane-sugar.

It was thought advisable, as in the case of raw cane-sugars, to study first the effect of temperature upon the polarization of exhausted beet molasses and then calculate what the effect would be upon mixtures of this molasses and sucrose crystals as was done in the case of cane molasses.

Influence of Temperature upon the Polarization of Sugar Beet Molasses.—For the purpose of this work three samples of molasses from various American beet sugar factories, kindly supplied by the Bureau of Chemistry, Washington, D. C., were examined in accordance with the method previously described. The results of the work are shown in Table XII.

Table XII.

(Showing Composition of Beet Molasses and Influence of Temperature upon Polarization.)

No.	Polarization. Direct.	Polarization. Invert	Sucrose by Clerget.	Sucrose. Per cent.	Raffinose. Per cent.	Invert sugar. Per cent	Ash. Per cent.	Water. Per cent.	N. Bases, gums, etc. Per cent.	Change in polarization, 1° C. increase.
1	49.80	—16 50	50.18	50.07	....	0.64	8 99	17.00	23.30	0.0000
2	50.00	—13 62	48.43	46.79	1.74	0.65	7.97	20.03	22.82	—0.0113
3	53.87	12 24	50.04	47.53	3.41	1.53	5.89	22.54	19.10	—0.0045
Av....	51.22	- 14 12	49.55	48.13	1.72	0 94	7.62	19.86	21.74	—0.0053

The increase in direct polarization over the sucrose by Clerget in two of the samples would indicate an appreciable amount of raffinose. The percentages of sucrose and raffinose were calculated by Creydt's formula. The average composition of the above molasses agrees closely with that of European beet sugar factories.

The effect of temperature upon the polarization of beet molasses is seen to be almost negligible, there being a decrease of only 0.0053° V. for each degree C. increase in temperature. The calculated value for the sucrose of the average beet molasses would be —0.0144 and for the levulose +0.0041, leaving a difference of —0.0103, which is about double the value found experimentally. The effect of temperature upon the polarization of raffinose and the other constituents of beet molasses was not investigated.

Table XIII.

(Showing Influence of Temperature upon the Polarization of Calculated Mixtures of Sucrose Crystals and Exhausted Beet Molasses)

Per cent. sucrose crystals	Per cent. molasses.	Polarization.	Sucrose Per cent	Invert sugar Per cent	Raffinose. Per cent.	Temperature factor. Actual. Degree V.	Temperature factor. By formula 0.0003P. Degree V
100.00	0.00	100.00	100 00	0.00	0.00	—0.0300	—0.0300
90.00	10.00	95.00	94.80	0.10	0.15	—0.0275	—0.0285
80.00	20.00	90.00	89 60	0 20	0.30	—0 0250	—0.0270
70.00	30.00	85.00	84.40	0.30	0.45	—0.0225	—0.0255

Determination of the Influence of Temperature upon the Polarization of Raw Beet Sugars.—The calculation of the influence of temperature upon the polarization of mixtures of sucrose crystals and beet molasses is indicated by a few examples in Table XIII. The calculation was made in the same manner as described under cane molasses.

The application of the correction formula is thus seen to give results which are but little higher than would be actually obtained. This conclusion was verified by determination of the temperature factor upon 5 raw domestic beet sugars.

Table XIV.

(Showing the Influence of Temperature upon the Polarization of Raw Beet Sugars.)

No.	Polarization 20° C.	Temperature factor (change per 1° C. increase). Found.	By formula 0.0003P.
1	93 20	—0.0220	—0.0280
2	91.25	—0.0276	—0.0274
3	89.00	—0.0205	—0.0267
4	86.60	—0.0263	—0.0260
5	85.50	-0.0214	—0.0257
Average......	89.11	—0.0236	—0.0267

The above temperature factor found for an average beet sugar of 89 polarization agrees closely with that calculated in Table XIII. We are therefore probably safe in saying that the application of the formula $P^{20°} = P^t[1 + 0.0003\ (t - 20)]$ to the polarization of raw beet sugars will give very closely the polarization that would be obtained under standard conditions. This of course would not hold for such beet sugars as contained much reducing sugar.

CONCLUSION.

It has been shown in the foregoing pages (1) from the theoretical consideration of the effect of temperature upon the specific rotation of sucrose and levulose, (2) from a consideration of the effect of temperature upon the polarization of mixtures of sucrose and sugar-cane molasses, and (3) by actual experiment that no temperature correction established for the changes in specific rotation of sucrose can be applied successfully to the polarization of raw cane products. A question which still remains to be considered is whether any kind of temperature correction can be adopted that will give the polariscope reading obtainable under standard conditions.

The first method which suggests itself for this purpose is a diminishing scale of corrections such

as that of Table XI, or the diagram, said corrections (for increase in temperature) to be added to sugars polarizing over 80 and to be subtracted from those polarizing below 80. The use of such a system would be unquestionably more accurate for cane products than any method of correction based upon changes in the specific rotation of sucrose alone and in the long run could be regarded as perfectly just. The great objection to its use, as with all other methods, is that it would not give the true correction for many individual samples of sugar, whose composition, especially as regards invert sugar and moisture, is different from the average type. Any method or scheme of analysis which works injustice to no matter how small a percentage of the trade should meet with disfavor as long as there exists a method which will work absolute justice to all.

A second remedy for the difficulties of temperature is suggested by that provision of the International Commission upon Uniform Methods of Sugar Analysis, which states that when "the temperature is higher than 20° saccharimeters may be adjusted at 30° or any other desired temperature providing that the analysis of sugar be made at the same temperature." This adjustment of saccharimeters to temperature above 20° may be made in several ways. It can be accomplished by changing the quartz wedges of the instrument, or by increasing the normal weight of sugar, or by increasing the length of the observation tube or in any other way that will enable the scale of the saccharimeter to indicate 100 when pure sucrose is polarized at the specified temperature. When only local polarizations and comparisons are involved it may be advantageous to make some such adjustment as the above. But for the broader work of comparison between distant points, as between the tropics and northern latitude, polarizations should be performed under one uniform set of standard conditions and the use of different temperatures of standardization is not advisable,[1] since comparisons are no longer possible upon a large class of low-grade saccharine products. The same difficulty is introduced as in the correction of polarizations by the formula $P^{20°} = P^t[1 + 0.0003\ (t - 20)]$ or by the sucrose values of quartz plates. Two saccharimeters, for example one standardized for the rotation of sucrose at 20° and one standardized for the rotation of sucrose at 30°, will give of course identical results for pure sucrose, but not for a raw cane-sugar, nor for a cane molasses, nor for a large class of other products. While the change in specific rotation of sucrose has been corrected, the changes in the specific rotation of the levulose and other impurities have not been equalized. Having adjusted a saccharimeter to any desired temperature, this standard temperature must be rigidly adhered to, if identical observations are always to be obtained between different chemists.

[1] The inadvisability of introducing different standards for saccharimeters is fully discussed by Prinsen Geerligs in "*De Indische Mercuur*," April 13, 1909. "*Temperatuurs-correctie bij de Polarimetrische Gehaltebepaling van Rietsuiker.*"

The solution of the problems of temperature in the polarization of raw sugars and other products resolves itself then into simply this: If we are to make temperature corrections in the polarization of commercial products, we must correct for variations in the specific rotations of all the ingredients therein present. If it is impossible to do this no temperature corrections at all should be attempted, but all polarizations should be made as nearly as possible under standard conditions. Custom House laboratories, Arbitration laboratories, and all other laboratories, upon the results of which great interests are involved, should be equipped with cooling and warming apparatus for maintaining a uniform standard temperature throughout the year.

The opinion of Judge Townsend of the Circuit Court in the case of the Importers of Sugar *vs.* the United States—that if the Government desires to secure uniformity and accuracy in the polarizations of sugars, tests should be made at the temperature at which the instruments are standardized—has already been quoted. As an expression of absolute justice and of scientific truth that opinion cannot be reversed, although the decision of this Court, as we have seen, was afterwards set aside by the Court of Appeals.

The services rendered to science by the researches of the many chemists who have investigated the influence of temperature upon the specific rotation of sucrose are great; the results of their labors are lasting and will stand the test of time. The application, however, of what they have established for pure sucrose to the polarization of all grades of saccharine products is a misapplication. It is a great mistake. It will increase rather than diminish the errors between many of the saccharimetric observations of different analysts and is bound to work great injustice when applied commercially.

[From the Laboratory of Physiological Chemistry, Department of Animal Husbandry, University of Illinois.]

CHEMISTRY OF FLESH.

[EIGHTH PAPER.][1]

A PRELIMINARY STUDY OF THE EFFECT OF COLD STORAGE UPON BEEF AND POULTRY.

(SECOND COMMUNICATION.)

By A. D. Emmett and H. S. Grindley

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In connection with the previous study upon the influence of cold storage upon uncooked beef and poultry it was thought that it would be of economic and scientific interest to make several cooking experiments upon some of the fresh and refrigerated uncooked samples and thereby to ascertain what influence, if any, the cooked meats might show over the uncooked, as to the changes brought about during cold storage. It could easily be assumed that the process of refrigeration would produce not only chemical but also physical changes in the meats which might not be apparent upon simply analyzing the uncooked product but would be brought out more distinctly by analyzing the cooked samples and the resulting broths and drippings. With this object in view, both boiling and roasting experiments were made upon portions of the same samples of the uncooked loin cuts, laboratory numbers 1969 and 1988, which were studied in the preceding[2] paper. The former cut was held in storage for 6 days and the latter one for 43 days, both at approximately 33°–35° F.

The literature pertaining to the influence of cold storage upon both uncooked and cooked flesh was given in our former paper.

EXPERIMENTAL.

For this study, upon the comparative losses and chemical changes resulting in the cooking of refrigerated meat, held in cold storage for varying lengths of time, eight cooking experiments were carried out. The same methods of cooking meats as were formerly[3] used in this laboratory were followed. The samples were obtained from the finely chopped and well mixed lean portion of the cuts of the uncooked loin. In the first case, where the meat was kept in storage for 6 days, the following cooking experiments were made:

Experiment 1.—Boiling at 85° C. 1000 grams of the chopped meat were taken, properly prepared and then plunged into 2000 cc. of distilled water, the temperature of which was maintained at 85° C. The time of cooking was 3 hours. This experiment was done in duplicate. The samples were designated Nos. 1966 and 1967.

Experiment 2.—Boiling at 100° C. 1000 grams of the sample were used. It was prepared and then placed in 2000 cc. of vigorously boiling water and cooked thus for 3 hours. The evaporated water was replaced from time to time. This test was also done in duplicate, the samples being designated Nos. 1968 and 1977.

Experiment 3.—Roasting at 195° C. 1000 grams of the finely divided beef were prepared for roasting in the gas oven. The temperature for the first 15 minutes was 250° C. and for the remaining time 195° C. The meat was cooked until the inner temperature[1] reached 60° C. In this case the total time of roasting was 1 hour. The sample was given laboratory number 1978.

Experiment 4.—Roasting at 100° C. 1000 grams of the beef loin sample were roasted in the Aladdin oven. The preliminary searing was done in the gas over at a temperature of 250° C. for 15 minutes. The meat was then transferred to an Aladdin oven and cooked at 100° C. until the inner temperature reached 60° C. The time of cooking was 1 hour and 50 minutes. The cooked product was designated as No. 1979.

For the second series of four cooking experiments upon the beef loin which was held in cold storage for 43 days, exactly the same tests were carried out in detail. The time required to cook the gas roast until the inner temperature reached 60° C. was 1 hour, and the Aladdin roast, to the same degree, was 2 hours and 20 minutes.

In preparing the above samples for cooking, the weighed portions were made into loaves of as nearly the same shape and size as possible. The meats for the boiling tests were wrapped with pieces of cheese-cloth. All the samples were prevented from touching the bottom of the cooking vessels and so arranged that the heat and water could penetrate all sides of the loaves.

CHEMICAL METHODS USED.

In analyzing the cooked meats, the same chemical methods were followed as in the case of the un-

[1] H. S. Grindley, *Jour. Amer. Chem. Soc.*, **26**, 1086 (1904). H. S. Grindley and A. D. Emmett, *Ibid.*, **27**, 658 (1905). A. D. Emmett and H. S. Grindley, *Ibid.*, **28**, 25 (1905). P. F. Trowbridge and H. S. Grindley, *Ibid.*, **28**, 469 (1906). H. S. Grindley and H. S. Woods, *Journ. of Biol. Chem.*, **2**, 309 (1907). A. D. Emmett and H. S. Grindley, *Ibid.*, **3**, 491 (1907). A. D. Emmett and H. S. Grindley, This Journal, **1**, 413 (1909).

[2] *Loc. cit.*

[3] Grindley, *U. S. Dept. Agr., O. E. S., Bull.* **102** (1901). Grindley and Mojonnier, *Ibid.*, **141** (1904). Grindley and Emmett, *Ibid.*, **162** (1905).

[1] Sprague and Grindley, *University Studies*, **2**, 4.

cooked cold storage samples, that is, the cold water extraction and the subsequent separation of the various constituents was undertaken.

In the case of the broths from the boiled meats, the same soluble constituents were determined in the clear filtrates as were estimated in the cold water extracts of the uncooked and cooked meats. The residues left upon the filter were analyzed for the insoluble protein and the fat. The data thus obtained, as regards the various constituents, were directly comparable with those from the cooked meat and gave a means of determining the nature of the loss of these several constituents.

The drippings from the roasted meats were thoroughly extracted with hot water, and the extracts were measured, filtered, and analyzed in exactly the same manner as the broths. In this way the soluble and insoluble portions were separated and the analysis was thus obtained upon a basis similar to that of the corresponding cooked meats.

The total losses resulting from the cooking of the samples were ascertained by transferring the meats, while still warm, to tared glass covered jars. After allowing several hours for the samples to cool in the refrigerator, they were weighed and the losses calculated. By this means of cooling the meats, the usual continued loss of moisture after removal of the hot cooked product was reduced to a minimum.

It should be stated again in connection with the chemical analysis, that at the time of making this preliminary study upon cold storage flesh, the methods of determining creatin,[1] ammonia,[2] and total acidity were not sufficiently developed for use.

DISCUSSION.

The data relating to the results obtained from the cooking tests are given for the meats, in Table I (calculated to the fresh substance), in II (calculated to the fat-free substance), and in III (calculated to the same water content as the corresponding samples held in storage for the shorter period), and for the broths and drippings in Table IV (calculated in per cent. of the uncooked meats), and in V (calculated in respect to the proportional distribution of the several constituents).

CHEMICAL COMPOSITION OF THE COOKED MEATS.

In referring to the data for the meats, it will be seen in the case of the boiled samples, which were held in storage for 6 days, that the results are reported as the average of two tests. For example, in the sample cooked at 85° C., the data represent the average of laboratory numbers 1966 and 1967. The object of carrying out the duplicate tests in these two cases was to ascertain just what might be our criterion as to the actual influence of cold storage, whether the differences which might appear to be due to refrigeration were not really a resultant of the errors arising from the method of cooking. A study of these data showed, when calculated upon the fresh basis, that the duplicate samples did not correspond very well in several of their percentage constituents. This was most marked, perhaps, in the case of the water, where samples 1966 and 1967 were respectively 61.95 and 61.24 per cent., and samples 1968 and 1977 were each 60.96 and 62.35 per cent., making a difference in the former case of 0.71 per cent. and in the latter of 1.39 per cent. These dissimilarities in the moisture content of the cooked meats are not at all surprising, especially in the case of boiled meats. However, in following out the same general plan of calculating these data as was done for the uncooked meats, namely to the fat-free basis and then to the same water content it was found, in each case, that the respective tests agreed quite well.

It is obvious from the above statements that it will be best, in our detailed study of the influence of cold storage, to consider the data relating to the cooked meats, in these several cooking experiments, as calculated from the fat-free substance and then to the same water content as the meats held in storage for the shorter period. However, a brief survey of the results as calculated to the fresh substance, Table I, will be of interest in bringing out certain facts which do not seem to have been influenced in the main by either the moisture or the fat content.

Chemical Composition of Cooked Beef Loin, Calculated upon the Fresh Basis.

The percentage of soluble dry substance was found to be higher throughout for the samples which had been kept in storage 43 days, but in the case of the roast (195° C.), the difference was so slight as to be neglible, However, if allowance was made for the soluble ash, the resulting soluble organic matter was found to be greater in all the cooked samples which were kept for 43 days.

[1] Grindley and Woods, *J. Biol. Chem.*, **2**. Emmett and Grindley, *Ibid.*, **3**.

[2] Gill and Grindley, *Science*, **27**.

In the case of boiled meats, the percentage increase amounted to 20.9 for the 85° C. and 12.1 for the 100° C. sample, and for the roasted meats 5.4 per cent. in the case of the gas-cooked and 13.9 per cent. in the Aladdin-cooked sample. The next most striking difference to be brought out is shown in the percentage of coagulable nitrogen and protein. The samples for the two boiled and the gas-roasted meats obtained from the 43-day stored samples are utterly absent of this constituent. The Aladdin-roasted meats, however, sample, varying with a difference of 1.96 per cent. in the meat boiled at 85° C. to only 0.19 per cent. in 100° C. boiled meat. The variation in moisture content accounts for this wide range as will be shown subsequently. The total organic extractives were higher in every case in the meats kept for the longer period, being in per cent. of their total amounts 20.5, 30.0, 11.2, and 10.7, respectively, for the meats boiled at 85° and 100° C., and those roasted at 195° and 100° C. The total soluble nitrogen was higher in the samples which

Table I.

Chemical Composition of Cold Storage Flesh. Lean Beef Loin, Cooked.

(Calculated to the Fresh Substance.)

Description of sample	Boiled at 85° C. 3 hours.		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour.		Roasted at 100° C.	
							1⅝ hrs.	2⅓ hrs.
Laboratory No.	1966–67	1989	1968–77	1990	1987	1991	1979	1992
Time held in cold storage (days)	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	61.60	63.03	61.66	59.53	63.66	64.95	65.68	65.55
Dry substance:								
Soluble	3.05	3.56	2.84	3.18	4.37	4.42	4.27	4.63
Insoluble	35.70	33.43	35.87	37.60	32.52	31.06	30.50	30.38
Total	*38.75*	*36.99*	*38.71*	*40.78*	*36.89*	*35.48*	*34.77*	*35.01*
Protein:								
Soluble coagulable	0.09	None	0.14	None	0.16	None	0.49	0.53
Soluble non coagulable	0.16	0.30	0.44	0.34	0.18	0.41	0.12	0.25
Total	*0.25*	*0.30*	*0.58*	*0.34*	*0.34*	*0.41*	*0.61*	*0.78*
Insoluble	25.37	23.36	26.33	26.38	23.19	21.73	21.46	20.90
Total	*25.62*	*23.66*	*26.91*	*26.72*	*23.53*	*22.14*	*22.07*	*21.68*
Organic extractives:								
Nitrogenous	0.90	1.08	0.75	0.99	1.23	1.22	1.11	1.26
Non-nitrogenous	1.20	1.45	0.92	1.18	1.74	1.86	1.59	1.73
Total	*2.10*	*2.53*	*1.67*	*2.17*	*2.77*	*3.08*	*2.70*	*2.99*
Fat	10.14	9.85	9.32	11.01	9.22	9.12	8.95	9.25
Ash:								
Soluble	0.71	0.73	0.60	0.67	1.06	0.93	0.96	0.86
Insoluble	0.19	0.22	0.22	0.21	0.11	0.21	0.09	0.23
Total	*0.90*	*0.95*	*0.82*	*0.88*	*1.17*	*1.14*	*1.05*	*1.09*
Nitrogen:								
As soluble coagulable protein	0.014	None	0.022	None	0.026	None	0.078	0.084
As soluble non-coagulable protein	0.027	0.048	0.071	0.055	0.028	0.066	0.019	0.040
Total	*0.041*	*0.048*	*0.093*	*0.055*	*0.054*	*0.066*	*0.097*	*0.124*
As soluble non-protein substance	0.287	0.346	0.238	0.316	0.395	0.391	0.355	0.404
Total	*0.328*	*0.394*	*0.331*	*0.371*	*0.449*	*0.457*	*0.452*	*0.528*
Insoluble	4.059	3.738	4.214	4.220	3.710	3.476	3.434	3.345
Total	*4.387*	*4.132*	*4.545*	*4.591*	*4.159*	*3.933*	*3.886*	*3.873*
Phosphorus:								
Soluble inorganic	0.096	0.128	0.093	0.120	0.127	0.145	0.129	0.142
Soluble organic	0.048	0.025	0.031	0.026	0.054	0.045	0.047	0.044
Total	*0.144*	*0.153*	*0.124*	*0.146*	*0.181*	*0.190*	*0.176*	*0.186*
Insoluble	0.073	0.092	0.073	0.093	0.074	0.065	0.060	0.051
Total	*0.217*	*0.245*	*0.107*	*0.239*	*0.255*	*0.255*	*0.230*	*0.237*

showed a percentage of this constituent which was even a little higher than the samples from the 6-day storage meats. This difference may have been due either to the more moderate temperature of cooking or to the fact that the sample from the 43-day cold storage meat was kept in the oven 30 minutes longer, in order to allow the inner temperature to reach the same point as that of the corresponding sample from the 6-day cold storage meat. The total protein showed throughout a tendency to be lower in the 43-day were gotten from the 43-day stored meat, showing respectively an increase, calculated in per cent. of the total gain, of 20.1, 12.1, 1.8, and 16.8 for the boiled and roasted meats. Concerning the different forms of phosphorus, the soluble inorganic was distinctly higher throughout, showing a gain of 33.3 per cent. for the 85° C. boiled, 29.0 per cent. for the 100° C. boiled, 14.1 per cent. for the 195° C. roasted, and 10.0 per cent. for the 100° C. roasted meat. The organic phosphorus showed a tendency to be lower in the meat cooked

from the samples which were held in storage for the longer period but this was so slight in some cases, considering the indirect method of obtaining this particular data, that nothing can be said regarding it. Of the total soluble phosphorus, it may be stated that, on the average, it was slightly higher in the 43-day samples of cooked meat. A distinctive feature for the boiled and roasted meats is here shown in connection with the insoluble and total phosphorus. The former showed a gain on an average for the boiled meat from the 43-day sample of 26.7 per cent. and for the roasted meat a loss of 13.6 per cent. On the other hand, the boiled meats from the sample which was stored 43 days were also high in total phosphorus, showing a percentage total gain of 13.0 and 21.3, respectively, for the 85° C. and 100° C. samples, while the roasted meats were almost identical in both cases.

From the statements just made in comparing the cooked meats, which were obtained from samples kept in cold storage for 6 and 43 days, it may be stated, when considered upon the fresh basis, that they correspond to the uncooked meats in several respects, showing that the products which were held for the longer period were richer in soluble dry substance, organic extractives, and soluble inorganic phosphorus. Nothing further can be said of this data in this form in regard to the other constituents, the variations being rather inconsistent on account of the differences in moisture and fat content.

In studying the data of the cooked meats, calculated to the fat-free basis, as in Table II, it will be seen that they show the same general facts as just cited. Therefore, it will not be of any special interest to enter into any discussion of the figures in this connection and our attention will be directed to a study of the data calculated to the fat-free basis and thence to the same water content, as given in Table III. Here, it will be seen that the respective cooked samples, designated as being from the meat held for 43 days, are calculated in each case to the same percentage moisture

TABLE II.

CHEMICAL COMPOSITION OF COLD STORAGE FLESH. LEAN BEEF LOIN, COOKED.

(Calculated to the Fat-free Basis.)

Description of sample	Boiled at 85° C. 3 hours.		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour.		Roasted at 100° C.	
							1 5/8 hrs.	2 1/8 hrs.
Laboratory No.	1966–67	1989	1968–77	1990	1978	1991	1979	1992
Time held in cold storage (days)	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	68.29	69.91	67.72	66.66	69.70	71.13	71.78	71.79
Dry substance:								
Soluble	3.38	3.95	3.12	3.56	4.78	4.84	4.67	5.07
Insoluble	28.33	26.14	29.16	29.78	25.52	24.03	23.55	23.14
Total	*31.71*	*30.09*	*32.28*	*33.34*	*30.30*	*28.87*	*28.22*	*28.21*
Protein:								
Soluble coagulable	0.10	None	0.15	None	0.17	None	0.54	0.58
Soluble non-coagulable	0.18	0.33	0.49	0.38	0.20	0.45	0.13	0.27
Total	*0.28*	*0.33*	*0.64*	*0.38*	*0.37*	*0.45*	*0.67*	*0.85*
Insoluble	28.12	25.90	28.92	29.54	25.39	23.80	23.45	22.89
Total	*28.40*	*26.23*	*29.56*	*29.92*	*25.76*	*24.25*	*24.12*	*23.74*
Organic extractives:								
Nitrogenous	1.00	1.20	0.82	1.11	1.35	1.33	1.21	1.38
Non-nitrogenous	1.33	1.61	1.01	1.32	1.90	2.04	1.74	1.89
Total	*2.33*	*2.81*	*1.83*	*2.43*	*3.25*	*3.37*	*2.95*	*3.27*
Ash:								
Soluble	0.79	0.81	0.66	0.75	1.16	1.02	1.05	0.94
Insoluble	0.21	0.24	0.24	0.24	0.12	0.23	0.10	0.25
Total	*1.00*	*1.05*	*0.90*	*0.99*	*1.28*	*1.25*	*1.15*	*1.19*
Nitrogen:								
As soluble coagulable protein	0.016	None	0.024	None	0.028	None	0.086	0.092
As soluble non-coaguable protein	0.030	0.053	0.78	0.061	0.031	0.072	0.020	0.044
Total	*0.046*	*0.053*	*0.102*	*0.061*	*0.059*	*0.072*	*0.106*	*0.136*
As soluble non-protein substance	0.138	0.384	0.261	0.354	0.433	0.428	0.388	0.442
Total	*0.364*	*0.437*	*0.363*	*0.415*	*0.492*	*0.500*	*0.494*	*0.578*
Insoluble	4.499	4.144	4.628	4.726	4.062	3.807	3.753	3.663
Total	*4.863*	*4.581*	*4.991*	*5.141*	*4.554*	*4.037*	*4.247*	*4.241*
Phosphorus:								
Soluble inorganic	0.106	0.142	0.102	0.134	0.139	0.159	0.141	0.155
Soluble organic	0.053	0.028	0.034	0.029	0.059	0.049	0.051	0.049
Total	*0.159*	*0.170*	*0.136*	*0.163*	*0.198*	*0.208*	*0.192*	*0.204*
Insoluble	0.081	0.102	0.080	0.105	0.081	0.071	0.066	0.056
Total	*0.240*	*0.272*	*0.216*	*0.268*	*0.279*	*0.279*	*0.258*	*0.260*

content as those for 6 days. Further, it was thought feasible to present an average of the four tests for each of these meats and thus eliminate in part the individuality, and thereby get a general deduction, if possible. The two columns at the right of the table give these averaged data.

Chemical Composition of Cooked Beef Loin, Calculated to the Same Water Content.

In taking up a detailed study of the constituents, the soluble dry substance showed a higher percentage composition for the samples held in storage for 43 days, varying from 23.1 per cent. in the case of the meat boiled at 85° C. to 6.3 per cent. for the one roasted at 195° C., and gave an average gain for all of 11.3 per cent. This gain was due chiefly to the greater per cent. of nitrogenous and non-nitrogenous organic extractives in these samples but in some instances, as in the boiled meats, it was also influenced slightly by the soluble ash. Naturally, the insoluble dry substance must, of necessity, be correspondingly lower in the 43-day samples. This is most pronounced for the insoluble protein, the average results for the former, the dry substance, being a decrease of 1.7 per cent. of the whole, and for the latter, the protein, one of 2.0 per cent.

As was stated in considering the data upon the fresh basis, the coagulable protein is absent in the boiled and the gas-roasted meats from the composite 43-day cold storage samples, but it is a trifle higher for the Aladdin roasts, being 0.54 and 0.58 per cent., respectively, for the meats from the 6- and 43-day samples. On an average, the results showed the coagulable protein to be 0.24 per cent. for the tests with the 6-day cold storage meat and 0.14 per cent. for the tests with the 43-day stored sample or almost two times as great in the former case. The non-coagulable and total soluble protein showed no consistent variations. In some cases, they were higher

TABLE III.

CHEMICAL COMPOSITION OF COLD STORAGE FLESH, FAT-FREE SUBSTANCE. LEAN BEEF LOIN, COOKED.

(Calculated to the Same Water Content.)

Description of sample	Boiled at 85° C. 3 hours.		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour		Roasted at 100° C. 1 5/6 hrs	Roasted at 100° C. 2 1/3 hrs.	Average of (4).	Average of (4).
Laboratory No.	1966–67	1989	1968–77	1990	1978	1991	1979	1992		
Time held in cold storage (days)	6	43	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	68.29	68.29	67.72	67.72	69.70	69.70	71.78	71.78	69.37	69.37
Dry substance:										
Soluble	3.38	4.16	3.12	3.45	4.78	5.08	6.67	5.07	3.99	4.44
Insoluble	28.33	25.55	29.16	28.83	25.52	25.22	23.55	23.15	26.64	26.19
Total	*31.71*	*31.71*	*32.28*	*32.28*	*30.30*	*30.30*	*23.22*	*28.22*	*30.63*	*30.63*
Protein:										
Soluble coagulable	0.10	None	0.15	None	0.17	None	0.54	0.58	0.24	0.14
Soluble non coagulable	0.18	0.35	0.49	0.37	0.20	0.47	0.13	0.27	0.25	0.37
Total	*0.28*	*0.53*	*0.64*	*0.37*	*0.37*	*0.47*	*0.67*	*0.85*	*0.49*	*0.51*
Insoluble	28.12	27.29	28.92	28.60	25.39	24.98	28.45	22.90	26.47	25.94
Total	*28.40*	*27.64*	*29.56*	*28.97*	*25.70*	*25.45*	*24.12*	*23.75*	*26.96*	*26.45*
Organic extractives.										
Nitrogenous	1.00	1.26	0.82	1.08	1.35	1.40	1.21	1.38	1.09	1.28
Non-nitrogenous	1.33	1.70	1.01	1.28	1.90	2.14	1.74	1.89	1.49	1.75
Total	*2.33*	*2.96*	*1.83*	*2.36*	*3.25*	*3.54*	*2.95*	*3.27*	*2.59*	*3.03*
Ash.										
Soluble	0.79	0.85	0.66	0.73	1.16	1.07	1.05	0.94	0.91	0.90
Insoluble	0.21	0.25	0.24	0.23	0.12	0.24	0.10	0.25	0.17	0.24
Total	*1.00*	*1.11*	*0.90*	*0.90*	*1.48*	*1.31*	*1.15*	*1.19*	*1.08*	*1.14*
Nitrogen:										
As soluble coagulable protein	0.016	None	0.024	None	0.028	None	0.086	0.092	0.038	0.023
As soluble non coagulable protein	0.030	0.056	0.078	0.059	0.031	0.076	0.020	0.044	0.040	0.059
Total	*0.046*	*0.056*	*0.102*	*0.059*	*0.059*	*0.076*	*0.106*	*0.136*	*0.078*	*0.082*
As soluble non protein substance	0.318	0.404	0.261	0.343	0.433	0.449	0.388	0.442	0.350	0.409
Total	*0.364*	*0.460*	*0.363*	*0.402*	*0.492*	*0.525*	*0.494*	*0.578*	*0.428*	*0.491*
Insoluble	4.499	4.367	4.628	4.576	4.062	3.995	3.753	3.664	4.236	4.151
Total	*4.863*	*4.827*	*4.991*	*4.978*	*4.554*	*4.520*	*4.247*	*4.242*	*4.664*	*4.642*
Ratio of non protein to protein										
In water extract	1: 0.14	1: 0.14	1: 0.39	1: 0.17	1: 0.19	1: 0.17	1: 0.27	1: 0.31	1: 0.22	1: 0.20
In meats	1: 4.29	1: 10.91	1: 18.12	1: 13.52	1: 9.50	1: 9.06	1: 9.95	1: 8.62	1: 12.32	1: 10.53
Phosphorus:										
Soluble inorganic	0.106	0.150	0.102	0.130	0.139	0.167	0.141	0.155	0.122	0.150
Soluble organic	0.053	0.029	0.034	0.028	0.059	0.051	0.051	0.049	0.049	0.040
Total	*0.159*	*0.179*	*0.136*	*0.158*	*0.198*	*0.218*	*0.192*	*0.204*	*0.171*	*0.190*
Insoluble	0.081	0.106	0.080	0.101	0.081	0.074	0.066	0.056	0.077	0.084
Total	*0.240*	*0.287*	*0.216*	*0.259*	*0.279*	*0.292*	*0.258*	*0.260*	*0.248*	*0.274*

for the meats from the 43-day sample; in others, lower. The only thing that can be stated in this connection is that the slight differences in the non-coagulable protein indicate the absence of putrefactive changes in the samples kept for the longer period. The total protein showed a slightly lower per cent. for the cooked meat obtained from 43-day sample varying from 1.2 in the gas roast to 1.5 in the Aladdin roast, making an average decrease of 1.9 per cent. for all the cooked meats. This loss, while small in relation to the insoluble or total protein, is fully accounted for in the organic extractives where the nitrogenous form shows a percentage gain for the meat kept for the longer period of 26.0, 31.7, 3.7, and 14.0, respectively, for those boiled at 85° C. and 100° C., and those roasted at 195° and 100° C., and where the non-nitrogenous form shows similarly a gain of 27.8, 26.7, 12.6, and 8.6 per cent., making a corresponding increase for the total organic extractives of 27.0, 29.0, 9.0 and 10.9 per cent. Averaging these three constituents for all the cooked meats, it is seen that the nitrogenous extractives are 17.4 per cent., the non-nitrogenous 17.4 per cent., and the total 17.0 per cent. higher for the samples from the meat kept for 43 days. When it is borne in mind that these extractives are the constituents of the meat which contribute to some extent at least to the flavor of the cooked products and also act as stimulants to some of the gastric glands, it will be seen that these figures have a significant value and indicate again in a decided manner the change which takes place in the ripening of meats during cold storage.

Concerning the various forms of ash, little can be stated inasmuch as the changes were slight. There seems to have been a tendency for the soluble ash to be a trifle higher in the boiled meats, obtained from the 43-day stored sample, and to be lower in the corresponding roasted samples. The percentage of insoluble ash of the boiled meats is about the same for both samples but that for the roasted meats from the longer stored sample is about double the amount of those for the 6-day. As a result of these variances in the ash of the boiled and roasted meats, the percentage of total ash in the former was slightly higher for meats held in storage for the longer period, while in the latter, it was practically identical.

What was said of the soluble, coagulable, non-coagulable, total soluble, and insoluble protein apply here for the same forms of nitrogen, as do also the remarks relating to the non-protein nitrogen which, multiplied by 3.12, corresponds to the nitrogenous extractives. However, it may be of interest to notice the total soluble and total nitrogen. The first form of nitrogen was distinctly higher in every case for the cooked samples from the meats which had been stored for 43 days, being for the boiled meats, 26.4 per cent. for the one cooked at 85° C. and 10.7 per cent. for that cooked at 100° C., and for the roasted meats, 6.7 per cent. for the 195° C., and 17.0 per cent. for the 100° C. roast. Averaging these four, the percentage increase for the total soluble nitrogen will be found to be about 14.5 per cent. This higher percentage of soluble nitrogen was due primarily to the non-protein form, which in part seems to have been compensated for, in considering the total nitrogen of the meats, by the decrease in the insoluble form. The second form of nitrogen, the total, was slightly lower throughout for the meats from the 43-day sample, but calculating the differences in per cent. of the total amounts, it will be found that they ranged from 0.8 of one per cent. in the 195° C. roast, to 0.1 of one per cent. in the 100° C. roast, which brings the results within the limit of experimental error. This fact goes to show that as far as the total nitrogen is concerned the influence of hanging in cold storage was not apparent and it incidentally adds much to confirm the statement that like pieces of meat can be so cooked by the same method that the resulting data from the samples will be comparable when calculated to the proper basis.

It will be of interest to note in connection with this discussion of the forms of nitrogen, the values of the ratios of the non-protein nitrogen to the protein nitrogen, first in the water extract and second in the meats. The data given in the table show that there were but very slight differences between the proportion of non-protein to soluble protein nitrogen in the samples which were obtained from the 6- and 43-day storage meats, being so small as to be of no dietetic or economic value. On the other hand, regarding the ratio of the non-protein to the total protein nitrogen in the meat, which term includes the soluble and insoluble forms, it will be seen that there was a distinct difference, the meats from the 43-day sample being lower throughout. For example, in the 85° C. boiled meat, from the 6-day storage sample, the ratio was 1 : 14.3, and in that from the 43-day sample it was 1 : 10.9, in the 100° C. 6-day boiled

meat it was 1 : 18.1, and in the 43-day sample it was 1 : 13.5; in the 195° C. roast meat, it was 1 : 9.5 for the 6-day, and 1 : 9.1 for the 43-day sample, and finally in the 100° C. Aladdin roast, it was respectively 1 : 9.9 and 1 : 8.6 for the meats which had been in cold storage for 6 and 43 days. In averaging all the non-protein and total protein nitrogen in the two sets of samples, the ratio of the non-protein to the total protein is 1 : 12.3 for the meats obtained from the 6-day sample, and 1 : 10.5 for the cooked meats from the sample kept for 43 days. From these data, it seems that the nutritive value of the cooked meats which were from the sample kept in cold storage for 43 days, was lower than that from the samples which were from the meat held only 6 days. In other words, since the total nitrogen in each case remained practically the same, the changes which took place during the hanging in cold storage were of such a nature as to modify the forms of nitrogen by increasing the extractives and decreasing the proteins. Whether the difference in the true food value of the meats was compensated for or not, by the natural inference, that the meats kept for a longer time are of a better flavor, and hence more palatable on account of the increased amounts of extractives, and therefore more digestible, is only to be conjectured, but it would seem that this deduction would be logical in the light of our practical knowledge of the subject.

In the same connection, the greater percentage of soluble inorganic phosphorus in the meat obtained from the 43-day sample, will be of interest, since the data show that this form of phosphorus in these samples was 41.5 per cent. higher in the 85° C. boiled meat, 27.4 per cent. in the 100° C. boiled meat, 20.1 per cent. in the 195° C. roast meat and 9.9 per cent. in the 100° C. roast meat, making an average increase for all the cooked meats which had been previously held in storage 43 days of 23.0 per cent. Furthermore, the boiled meats from this sample were both richer in total soluble, insoluble, and total phosphorus, while the corresponding roasted meats contained more total soluble and total phosphorus, but less insoluble phosphorus.

From this discussion of the composition of the cooked meats, obtained from samples which were held in cold storage for different lengths of time, it is evident that many of the changes which appeared in the results of the uncooked meats have persisted in the cooked ones, even to a more marked extent in some cases. In taking the average of the two, 6- and 43-day, cold storage uncooked samples, which was given in the previous paper, and that of the four cooked samples from the respective 6- and 43-day cold storage samples, it will be seen that these data, calculated as they were to the fat-free basis and then to the same water content in each of the respective cases, showed striking resemblances, indicating again the nature of the changes which took place during the hanging in cold storage, or the result of the "ripening" of the meat. Thus, the soluble dry substance in the uncooked meat was 5.63 and 6.13 per cent. for the meats from the 6- and 43-day samples, while in the cooked samples it was 3.99 and 4.44 per cent., respectively, making a percentage gain in the former case of 8.9 and in the latter of 11.3. In the case of the insoluble protein, the raw meats for the shorter period contained 17.05 per cent. and those for the longer period 16.53, showing a percentage decrease of 3.0 per cent. while the insoluble protein of the cooked meats for the corresponding periods were 26.47 and 25.94 per cent., making a decrease of 2.0 per cent. Similarly, the total protein showed a percentage loss in the uncooked meats of 2.0 and in the cooked meats of 1.9. As regards the organic extractives, the cooked meats from the samples which had been in cold storage for 43 days showed a greater increase for the nitrogenous form, a less one for the non-nitrogenous form, and practically the same one for the total, than did the cooked meats: the nitrogenous form, calculated in per cent. of the total, being 17.4 per cent. for the cooked and 12.5 per cent. for the uncooked; the non-nitrogenous form being 17.4 per cent. for the cooked and 20.7 per cent. for the uncooked; and finally the total extractives being 17.0 per cent. for the cooked meats, and 17.3 per cent. for the uncooked meats. Of the forms of nitrogen not dwelt upon indirectly in considering the proteins and extractives, that of the total soluble is of interest. In the uncooked meats, it showed a gain for the 43-day sample of 8.8 per cent. while in the cooked meats from this sample, this increase amounted to almost double that of the uncooked, being 14.7 per cent. The ratio of the soluble non-protein nitrogen to the total soluble protein nitrogen shows nothing more in the one case than in the other; however, the difference in the ratios of the non-protein nitrogen to the total protein nitrogen in the meat appears

more markedly in the cooked than in the uncooked samples. For example, the ratio of the forms of nitrogen in the case of the cooked meats from the 6-day stored sample of loin was 1:12.3 and in that for those from the meat which was held in storage 43 days it was 1:10.5, whereas it was 1:9.1 and 1:8.1, respectively, for the 6- and 43-day uncooked meats. The percentage gain of soluble inorganic phosphorus was about the same in both the uncooked and cooked meats, being in the former 20.3 and in the latter 22.9. Comparing the other forms of phosphorus, the differences in the case of the individual uncooked meats were not consistent throughout. However, in comparing the average of the constituents of the cooked meats with those of the corresponding uncooked samples, it is seen that the total soluble phosphorus in both cases showed about the same relative distribution and differences between the 6- and 43-day samples, being for the uncooked 0.171 per cent. for the former, and 0.203 per cent. for the latter, and for the average of all the cooked meats from these samples 0.171 and 0.190 per cents., respectively. The insoluble phosphorus, on the other hand, showed a decrease for the sample from the 43-day storage meat of 80.1 per cent. in the uncooked loin, while there was an increase of 9.1 per cent. in the cooked meats. Further, the total phosphorus in the raw meat held in storage for the longer time was 15.4 per cent. less than that for the meat kept for the 6-day period. In the cooked meats, the total phosphorus showed a gain for samples from the meat which was held in storage 43 days, of 10.5 per cent.

Chemical Composition of the Broths and Drippings, and the Losses Resulting from Cooking the Meats.

It will now be of interest to study still further any differences which might have been the result of the influence of cooking the two kinds of meat—the 6- and 43-day stored samples. Here, the percentage loss in cooking, the composition of the broths and drippings, the composition of the meats when compared directly with the broths and drippings, the proportional distribution of the various constituents which passed into the broths and drippings, and also those which remained in the cooked meats, all seem to have a bearing upon the effect of the length of time of hanging meats in cold storage.

In Table IV, the chemical composition of the broths and drippings as well as the percentage loss in cooking are given in detail, calculated in per cent. of the uncooked meats. First, taking up the matter of the gross loss which resulted from the boiling or roasting of the samples, it will be seen from the data that all of the 43-day refrigerated, cooked, samples weighed more than the 6-day refrigerated, cooked meats, and therefore that the total losses were correspondingly less in the two sets of meat. Calculated in per cent., the gross losses of the 43- and 6-day samples were respectively for the meats boiled at 85°, 24.07 and 29.12; for those boiled at 100° C., 31.66 and 32.86; for those roasted at 195° C., 17.08 and 22.04; and for those roasted at 100° C., 14.24 and 16.37, the whole making an average percentage loss of 21.76 and 25.10, respectively. Those figures show a difference between the two meats ranging from 1.21 per cent. in those boiled at 100° C. to 5.05 per cent. in the samples bo led at 85° C., or in considering the average, a difference of 3.34 per cent. The fact that each of the 6-day samples of meat showed a greater or less tendency to lose more upon cooking than did the 43-day samples, would seem to be pretty good evidence that the longer period of hanging caused some change in the chemical nature or physical structure of the meat which prevented the passage of as great a percentage of some of the constituents into the broths or drippings.

It will be of interest to study this point more in detail and in so doing, the chemical nature of the losses resulting from the cooking will be considered. It is evident that the losses just noted, refer to the cooked meats themselves and that, in reality, the so-called losses in cooking are generally utilized as broths, in the case of the boiled meats, and as gravy or drippings, in the case of the roasted meats. Therefore, the chemical composition of the broths and drippings must be considered in getting an insight into the detailed losses. Referring to this same table, IV, it will be seen that the composition of the broths and drippings is presented in exactly the same form as that for all the meats which have been studied thus far. This fact is of importance in that a much clearer insight can be had of the actual changes which take place in the cooking than if only the usual gross determinations were reported.

The first apparent differences in the nature of the losses is in the percentage of water. This term is somewhat general in that it refers to all

of the loss, other than that obtained as dry matter in the broths or drippings. In the case of the meats which were kept for the 43-day period, the losses from the cooked products showed that they contained less water, varying from 0.75 per cent. for the 100° C. boiled meat to 4.81 for the roast meat, and giving an average of 3.09 for all four tests. This indicates at once that the greatest difference in the total or gross loss was due to moisture, and if this be calculated, it will be found that 92.5 per cent. of the difference in the gross loss between the 6- and 43-day meats was actually due to the constituent water.

In the case of the dry substance, the differences were not so great, but yet considering the total amounts in each case, they were sufficient to state that the soluble and insoluble forms showed a lower percentage content throughout for the 43-day samples, averaging for the former a decrease over the loss in the 6-day sample of 10.5 per cent. and for the latter, one of 30.2 per cent., and making one of 15.9 per cent. for the total dry substance. The decrease of 10.5 per cent. in soluble dry substance seems to have been distributed in approximately the same proportion among the various soluble constituents, the proteins, the extractives and ash, so that it did not seem to produce any special difference in any one of the instances. For example, in the case of the boiled meats, the soluble protein of the broths seems to have been slightly lower while in the roasted meats the extractives of the drippings showed the greater percentage decrease. The average loss of 30.4 per cent. in the insoluble dry substance for the meats from the sample which was kept 43 days in storage was due chiefly to the lower percentage of fat which showed a loss varying from 39.3 per cent. in the 195° C. roast sample to 65.4 per cent. in the 100° C. boiled meat and averaging 60.0 per cent. for all the broths and drippings.

Aside from the insoluble and the soluble forms of the constituents that have been considered

TABLE IV.

CHEMICAL COMPOSITION OF COLD STORAGE FLESH. LEAN BEEF LOIN, COOKED.

(Calculated in Per cent. of the Uncooked Meat.)

Description of sample	Boiled at 85° C. 3 hrs.		Boiled at 100° C. 3 hrs.		Roasted at 195° C. 1 hr.		Roasted at 100° C.	
							1 5/6 hrs.	2 1/3 hrs.
Laboratory No.	1966–67	1989	1968–77	1990	1978	1991	1979	1992
Time held in cold storage, days	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	43.66	47.86	41.40	40.68	49.63	53.86	54.93	56.22
Dry substance:								
Soluble	2.16	2.70	1.91	2.17	3.41	3.67	3.57	3.97
Insoluble	25.30	25.38	24.08	25.69	25.35	25.75	25.51	26.05
Total	*27.46*	*28.08*	*25.99*	*27.86*	*28.76*	*29.42*	*29.08*	*30.02*
Protein:								
Soluble coagulable	0.07	None	0.09	None	0.12	None	0.41	None
Soluble non-coagulable	0.11	0.23	0.30	0.23	0.14	0.34	0.10	0.22
Total	*0.18*	*0.23*	*0.39*	*0.23*	*0.26*	*0.34*	*0.51*	*0.67*
Insoluble	17.97	17.73	17.67	18.02	18.08	18.02	17.95	17.92
Total	*18.15*	*17.96*	*18.06*	*18.25*	*18.34*	*18.36*	*18.46*	*18.59*
Organic extractives:								
Nitrogenous	0.64	0.82	0.50	0.68	0.96	1.01	0.93	1.08
Non-nitrogenous	0.84	1.10	0.62	0.80	1.36	1.54	1.33	1.48
Total	*1.48*	*1.92*	*1.12*	*1.48*	*2.32*	*2.55*	*2.26*	*2.50*
Fat	7.19	7.48	6.26	7.52	7.19	7.56	7.48	7.93
Ash:								
Soluble	0.50	0.55	0.40	0.46	0.83	0.77	0.80	0.74
Insoluble	0.14	0.17	0.15	0.14	0.08	0.17	0.08	0.19
Total	*0.64*	*0.72*	*0.55*	*0.60*	*0.91*	*0.94*	*0.88*	*0.93*
Nitrogen:								
As soluble protein	0.029	0.036	0.062	0.037	0.042	0.055	0.081	0.106
As soluble non-protein	0.203	0.263	0.160	0.216	0.308	0.324	0.297	0.346
Total	*0.232*	*0.299*	*0.222*	*0.253*	*0.350*	*0.379*	*0.378*	*0.452*
Insoluble	2.876	2.838	2.829	2.884	2.892	2.882	2.872	2.868
Total	*3.108*	*3.137*	*3.051*	*3.137*	*3.242*	*3.261*	*3.250*	*3.320*
Ratio of non-protein to protein:								
In water extract	1 : 0.14	1 : 0.14	1 : 0.39	1 : 0.17	1 : 0.55	1 : 0.17	1 : 0.27	1 : 0.31
In meats	1 : 14.3	1 : 10.9	1 : 18.0	1 : 13.5	1 : 9.5	1 : 9.1	1 : 9.9	1 : 8.6
Phosphorus:								
Soluble inorganic	0.068	0.097	0.063	0.082	0.099	0.120	0.108	0.122
Soluble organic	0.034	0.019	0.020	0.018	0.042	0.037	0.039	0.038
Total	*0.102*	*0.116*	*0.083*	*0.100*	*0.141*	*0.157*	*0.147*	*0.160*
Insoluble	0.052	0.070	0.049	0.063	0.058	0.054	0.050	0.043
Total	*0.154*	*0.186*	*0.132*	*0.163*	*0.199*	*0.211*	*0.197*	*0.203*

TABLE IV—(*Continued*).

CHEMICAL COMPOSITION OF COLD STORAGE FLESH. BROTH AND DRIPPINGS FROM LEAN BEEF LOIN, COOKED.

(Calculated in Per cent. of the Uncooked Meat.)

Description of sample	Boiled at 85° C. 3 hours		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour		Roasted at 100° C.	
							1 5/6 hrs	2 1/3 hrs.
Laboratory No.	1966–67	1989	1968–77	1990	1978	1991	1979	1992
Time held in cold storage (days)	6	43	6	43	6	43	6	43
Weight of uncooked meat (grams)	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
Weight of cooked meat (grams)	708.84	759.31	671.36	683.39	779.61	829.22	836.31	857.57
Gross loss in cooking:								
In grams	291.16	240.69	328.64	316.61	220.39	170.78	163.69	142.43
In per cent	29.12	24.07	32.86	31.68	22.04	17.08	16.37	14.24
	P. ct.	P. ct	P. ct.	P. ct.	P. ct.	P. ct.	P ct.	P. ct.
Water	27.22	22.43	29.92	29.17	21.33	16.52	15.67	13.66
Dry substance:								
Soluble	1.56	1.40	2.09	1.93	0.36	0.29	0.55	0.46
Insoluble	0.35	0.24	0.86	0.56	0.35	0.27	0.15	0.12
Total	*1.91*	*1.64*	*2.95*	*2.49*	*0.71*	*0.56*	*0.70*	*0.58*
Protein:								
Soluble coagulable	0.02	None	0.02	None	None	None	None	0.02
Soluble non-coagulable	0.24	0.19	0.36	0.33	0.13	0.11	0.19	0.19
Total	*0.26*	*0.19*	*0.38*	*0.33*	*0.13*	*0.11*	*0.19*	*0.21*
Insoluble	0.08	0.12	0.05	0.03	0.06	0.10	0.08	0.09
Total	*0.34*	*0.31*	*0.43*	*0.36*	*0.19*	*0.21*	*0.27*	*0.30*
Organic extractives:								
Nitrogenous	0.40	0.37	0.51	0.48	0.05	0.04	0.08	0.06
Non-nitrogenous	0.57	0.58	0.77	0.74	0.09	0.07	0.16	0.10
Total	*0.97*	*0.95*	*1.28*	*1.22*	*0.14*	*0.11*	*0.24*	*0.16*
Fat	0.27	0.12	0.81	0.28	0.28	0.17	0.06	0.03
Ash:								
Soluble	0.34	0.27	0.43	0.37	0.10	0.06	0.12	0.09
Insoluble	......	......	......	......	......	......	......	......
Total	*0.34*	*0.27*	*0.43*	*0.37*	*0.10*	*0.06*	*0.12*	*0.09*
Nitrogen:								
As soluble protein	0.041	0.030	0.061	0.053	0.020	0.018	0.030	0.031
As soluble non-protein	0.126	0.117	0.165	0.155	0.014	0.014	0.025	0.020
Total soluble	*0.167*	*0.147*	*0.226*	*0.208*	*0.034*	*0.032*	*0.055*	*0.051*
Insoluble	0.012	0.019	0.008	0.004	0.010	0.015	0.014	0.015
Total	*0.179*	*0.166*	*0.234*	*0.212*	*0.044*	*0.047*	*0.069*	*0.066*
Ratio of non-protein to protein:								
In water extract	1:0.33	1:0.26	1:0.37	1:0.34	1:1.43	1:1.25	1:1.18	1:1.56
Phosphorus:								
Soluble inorganic	0.041	0.043	0.055	0.057	0.011	0.011	0.013	0.014
Soluble organic	0.024	0.011	0.026	0.014	0.006	0.003	0.007	0.005
Total	*0.065*	*0.054*	*0.081*	*0.071*	*0.017*	*0.014*	*0.020*	*0.019*
Insoluble	......	......	......	......	......	......	......	......
Total	*0.065*	*0.054*	*0.081*	*0.071*	*0.017*	*0.014*	*0.020*	*0.019*

thus far, those of the nitrogen are of importance. The nitrogen of the drippings, from the roast meats, showed but very slight differences between the 6- and 43-day samples. The broths, however, showed the percentage of soluble protein nitrogen, the soluble non-protein, the total soluble and the total nitrogen to have been lower for the 43-day meats, on an average 18.6, 6.5, 9.7, and 8.4 per cent., respectively. The insoluble nitrogen varied but slightly and even then, inconsistently, and therefore showed nothing of value. The ratio of the soluble non-protein nitrogen to the soluble protein nitrogen showed no differences in the boiled meats and none in the roast meats which would indicate anything as to the nature of the losses due to length of time of storage.

The forms of phosphorus showed some interesting facts concerning the losses in cooking in connection with this study. This was especially true of the inorganic form which, contrary to all our previous discussion relative to the meats, did not show any noticeable differences in the case of the broth and drippings from the cooked meats obtained from the 6- and 43-day stored samples. The organic form which showed a greater percentage for the 6-day meats also showed a like state of affairs for the broths and drippings. When the total soluble phosphorus is considered; the 43-day samples were distinctly lower for the broths and but slightly lower for the drippings, averaging a decrease of 13.7 per cent. for all.

Having now considered the nature of the losses in detail, it will be of interest to compare them with the cooked meats, calculated upon the same basis, that is, in per cent. of the uncooked meats. In this way a further insight can be gotten as to the influence of the length of time of storage upon the cooking of meat.

The fact that 92.5 per cent. of the gross losses in cooking the meats was due to loss of moisture and that the meats from the 43-day samples lost less in cooking, would lead one to expect a higher percentage moisture content for these cooked meats. This condition appears to have existed in the case of the roasted meats and the ones boiled at 85° C., but in the case of the 100° C. boiled meats, there was a loss in favor of the samples from the 6-day storage meat, amounting to 0.72 per cent. Averaging all four of the tests, it was found that the meats obtained from the 43-day cold storage sample contained 2.24 per cent. more of water, or a total gain of 4.7 per cent., and it would therefore seem, as previously stated, that the cooked meats, from the samples kept in storage for the longer time, tended to be juicier.

The percentage of soluble dry substance of the samples from the 43-day storage meats was distinctly higher in every case, and it is significant to note that while the broths and drippings showed a corresponding decrease, yet this did not account for the entire gain. For example, in the meats boiled at 85° C., those from the 6-day sample contained 2.16 per cent. of soluble dry substance and those from the 43-day sample 2.70 per cent., making a difference of 0.54 per cent. or a percentage gain of 25.0. On the other hand, the broths from these meats showed the soluble dry substances to have been 1.56 per cent. in the meats from the 6-day sample and 1.40 per cent. in those from the 43-day meats, making a difference of 0.16 per cent. as compared with the 0.54 per cent. of the meats themselves. If allowances be made for this compensating percentage of 0.16, the cooked meats obtained from the 43-day storage sample still show a gain of 0.38 per cent. or 17.6 per cent. of the amount in the fresh 6-day samples. Applying this analogy to all the meats, the average showed the percentage of soluble dry substance to be respectively for the 6- and 43-day samples, 2.76 and 3.13 for the meats and 1.14 and 1.02 for the broth and drippings or an increase of 0.37 per cent. in the former and a decrease of 0.12 in the latter. This fact shows that the cooked meats from the 43-day storage sample were richer in soluble dry substance than those from the 6-day sample, even if no allowance was made for the greater percentage of water which the meats from the 43-day samples contained. It will be seen at a glance, upon considering the organic extractives, that they were the individual soluble constituents which cause the main differences. It will be recalled that the percentage of nitrogenous, non-nitrogenous, and total extractives were very nearly the same in the broths and drippings, obtained in cooking the meat from the 6- and 43-day storage samples, the latter showing the greater percentage loss for the 43-day samples. In the cooked meats, however, there was a decided percentage increase of the forms of extractives for the samples from the 43-day meat. This is more noticeable in the boiled than in the roasted ones. In the former the greatest percentage gains were in the 100° C. boiled meats for the nitrogenous and total extractives, being 36.0 and 32.0 per cent., respectively, and in the 85° C. cooked samples for the non-nitrogenous 31.0 per cent., and the 100° C. boiled for the total extractives 32.0 per cent. In the case of the roast meats, the average of the two tests showed that the samples from the 43-day storage meat were 10.5, 11.9, and 11.8 per cent. richer in nitrogenous, non-nitrogenous, and total extractives, respectively, than were those from the 6-day sample. If the two kinds of meat, the boiled and the roasted, the averaged, it will be seen, after deducting for the difference in the broth and drippings, that the nitrogenous extractives were 15.7 per cent., the non-nitrogenous 15.3 per cent. and the total 16.2 per cent. higher in the cooked meats from the 43-day sample.

In connection with such deductions as are apparent from the study of the forms of the extractives, it would be of interest to note the nature of the forms of protein in the cooked meats. It will be seen, as stated previously in another connection, that the cooked meats from the 43-day cold storage loin sample was lacking in coagulable protein, in the case of the boiled meats and in that roasted at 195° C. The samples roasted at 100° C. showed about the same percentage of the coagulable protein in the tests with the 6- and 43-day uncooked loin samples. If an average be made of all the meats, it will be found that the meats from the 6-day samples contained 0.17 per cent., and that those from the 43-day sample 0.11 per cent. The non-coagulable protein showed a tendency to be higher in meats from the 43-day sample. In the 100° C. boiled meats, this form of protein was slightly lower, being for the sample kept in storage 6 days 0.30 per cent., and for the one kept 43 days 0.23 per cent. The average of all the values showed a percentage of 0.16 for the sample from 6-day meats and 0.25 for that

from the 43-day samples. Associating with this fact, that on the average the non-coagulable protein was higher and the coagulable protein was lower in the cooked samples from the meats which were kept in cold storage for the longer period, with the fact that the uncooked meats when calculated to the fat-free and same moisture content were practically alike in these constituents, it seems very probable that during the process of cooking, the hydrolytic action was carried further with the samples from the 43-day cold storage meat and changed a part or all of the coagulable protein to the non-coagulable form. And if this statement is connected with the fact that the extractives were also higher, it is evident that the hydrolysis went beyond the protein stage and formed a greater percentage of the non-protein bodies.

Now comparing the percentage of the total soluble protein, the data show that the samples kept for 43 days were higher in the case of the meats boiled at 85° C. and also the meats roasted at 195° C., and 100° C., being 27.8, 30.8, and 31.4 per cent., respectively. On the other hand, the meat boiled at 100° C. showed a loss of total soluble protein for the sample obtained from the 43-day meat amounting to 41.0 per cent. of the total percentage in that from the 6-day sample. The average of all four meats shows a gain for those from the 43-day storage samples of 9.7 per cent., which, considering the small percentage of total soluble protein, actually amounts to only 0.03 per cent. of the samples themselves and therefore is of little nutritive significance. The percentage of insoluble protein showed but a slight difference between the various cooked meats kept for the two periods of storage. The greatest variation appeared in the case of the 100° C. boiled meat where the meats from the 43-day sample contained 18.02 per cent. and those from the 6-day sample 17.67 per cent., making a difference in favor of the former of 0.35 per cent. If the percentage of insoluble protein for all the samples for each period be averaged, it will be found that they were both the same, 17.92 per cent. The percentage of total protein was exceptionally close in each case in comparing cooked meats from the 6- and 43-day samples. The greatest differences were not over 1.0 per cent. of the amount determined and thus within the limit of the errors of the methods. It is therefore seen from the above discussion that there was very little difference between the actual nutritive values of the resulting cooked meats from the samples which were kept in cold storage for 6 and 43 days.

However, it will be of interest in this connection to study the various forms of nitrogen. What has been stated regarding the total soluble protein, nitrogenous extractives, and insoluble protein applies to these forms of nitrogen since each was simply multiplied by its conventional factor, to transform it to the above condition. Of the other forms of nitrogen, the total soluble of the cooked meats was higher in each case for the samples from the 43-day meat, ranging from 8.3 per cent. in 195° C. roast meat to 28.8 per cent. in the 85° C. boiled meat, and averaging for the four tests 16.9 per cent. The total nitrogen of the meats was but slightly higher for the samples kept in storage for the longer time, varying from 0.6 per cent. of the total amount in the 195° C. roast to 2.8 per cent. of that in the 100° C. boiled meat. Further, the ratio of the non-protein to the soluble protein nitrogen in the two classes of meats did not vary enough to be of any significance as to the influence of the length of time of storage, but in the case of the ratio of the soluble non-protein nitrogen to the total protein nitrogen, as was stated previously, the boiled meats showed a decided difference between the samples which were obtained from the 6- and 43-day cold storage meat, and the roast meats showed a similar, though less pronounced difference. In each of the cases, the ratio was less for the sample which was stored for the longer period, being respectively for the 6- and 43-day tests, for the meats cooked in water at 85° C. 1 : 14.3 and 1 : 10.9; for those cooked at 100° C., 1 : 18.0 and 1 : 13.5; and for those cooked by dry heat at 195° C., 1 : 9.5 and 1 : 9.1; and for those cooked at 100° C., 1 : 9.9 and 1 : 8.6. These data, regarding the forms of proteins, extractives, and nitrogen, indicate at first glance that the influence of cold storage resulted in producing cooked meats which were less nutritious when held in storage 43 days than when held but the 6 days, but bearing in mind the fact that the percentage of insoluble and total protein of the respective cooked meats were practically the same for those obtained from the 6- and 43-day samples, and also the fact that the percentage of nitrogenous organic extractives for non-protein nitrogen was higher for each of the samples from the 43-day meat, it will become evident why the ratios varied as they did and therefore it will be seen that the

cooked meats from the sample which was held in storage for the longer period were just as nutritious as those held for the shorter time, and also, that they were of a better flavor, due to the increased quantity of organic extractives.

The next constituents which should be considered are the fat and the forms of ash and phosphorus. The first showed a higher percentage content in the case of the cooked meats from 43-day samples varying from 5.1 per cent. in the 195° C. roast, to 20.1 per cent. in the 100° C. boiled meat, and upon averaging for all tests an increase of 8.4 per cent. In the percentages of soluble ash the variations for the boiled meat from the cold storage sample which was held 43 days showed a gain of 10.0 per cent. for the 85° C., and one of 15.0 per cent. for the 100° C., and for the roast meats, they indicated a loss of 7.2 per cent. for the 195° C. sample and one of 7.5 per cent. for the 100° C. sample. The insoluble ash for the boiled meats was about the same in the two cases but in the roasted meat, those from the 43-day stored sample were over twice as high in this form, being for the 195° C. roast 0.08 and 0.17 per cent., and for the 100° C. roast 0.08 and 0.19 per cent. for the samples from the 6- and 43-day cold storage meats, respectively. The percentage of total ash was somewhat higher in every case for the meat from the longer stored sample, being lowest in the 195° C. roast, 3.3 per cent., and highest in the 85° C. boiled sample, 12.5 per cent., and averaging for all 7.0 per cent.

The soluble inorganic phosphorus of the cooked meats which were from the 43-day sample showed a greater percentage content throughout than did those from the 6-day sample, being least for the 100° C. roast, 13.0 per cent. of the total amount, and greatest for the 85° C. boiled meat, 42.6 per cent., and averaging for all the four samples a gain of 24.5 per cent. This fact is of special note inasmuch as it will be recalled that the losses in cooking, the broths and drippings, showed no marked difference in this constituent, the meats from the 6-day samples containing no more inorganic phosphorus than did those from the 43-day samples. On the whole, little, if anything,

TABLE V.

PROPORTIONAL DISTRIBUTION OF THE NUTRIENTS IN THE COOKED MEATS DUE TO COOKING LEAN BEEF LOIN.

(Calculated in Per cent. of the Total Amounts in the Uncooked Meats, by Summation.)

Description of sample	Boiled at 85° C. 3 hours.		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour.		Roasted at 100° C.		Average of (4).	Average of (4).
							1 5/6 hrs.	2 1/3 hrs		
Laboratory No.	1966–67	1989	1968–77	1990	1978	1991	1979	1992	....	....
Time held in cold storage (days)	6	43	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	61.60	68.09	58.05	58.24	69.94	76.52	77.80	80.45	66.85	70.82
Dry substance:										
Soluble	58.10	65.85	47.75	52.93	90.45	92.67	86.65	89.62	70.74	75.27
Insoluble	98.64	99.06	96.55	97.87	98.64	98.96	99.42	99.54	98.31	98.86
Total	*93.50*	*94.48*	*89.81*	*91.80*	*97.59*	*98.13*	*97.64*	*98.11*	*94.63*	*95.63*
Protein:										
Soluble coagulable	77.80	None	81.82	None	100.00	None	100.00	95.75	89.90	23.94
Soluble non-coagulable	31.40	54.76	45.45	41.07	51.85	75.56	65.52	53.64	48.55	56.26
Total	*40.91*	*45.24*	*50.65*	*41.07*	*66.67*	*75.56*	*72.86*	*76.14*	*55.27*	*59.50*
Insoluble	99.56	99.33	99.72	99.85	99.67	99.45	99.56	99.50	99.63	99.53
Total	*98.16*	*98.30*	*97.68*	*98.08*	*98.97*	*98.87*	*98.56*	*98.41*	*98.34*	*98.41*
Organic extractives:										
Nitrogenous	61.54	68.91	49.50	58.62	95.05	96.19	92.08	94.74	74.54	79.59
Non-nitrogenous	59.60	65.48	44.60	51.95	93.80	95.65	89.26	93.67	71.81	76.69
Total	*60.41*	*66.90*	*46.67*	*54.82*	*94.31*	*95.87*	*90.40*	*94.12*	*72.95*	*77.93*
Fat	96.38	98.42	88.50	96.41	96.25	97.80	99.21	99.62	95.08	98.06
Ash:										
Soluble	59.52	67.07	48.19	55.42	89.25	92.77	86.96	89.16	70.98	76.10
Insoluble	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Total	*65.31*	*72.73*	*50.12*	*61.86*	*90.10*	*94.00*	*88.00*	*91.18*	*74.88*	*79.94*
Nitrogen:										
As soluble protein	41.27	54.82	50.64	41.11	67.36	75.55	73.26	77.48	58.13	62.24
As soluble non protein	61.75	69.19	49.23	58.22	95.56	95.80	92.23	94.59	74.69	79.57
Total	*58.13*	*67.06*	*49.02*	*54.88*	*90.98*	*92.24*	*87.38*	*89.01*	*71.53*	*70.05*
Insoluble	99.57	99.34	99.71	99.86	99.65	99.47	99.52	99.48	99.61	99.54
Total	*94.54*	*94.98*	*92.89*	*93.07*	*98.03*	*98.57*	*97.94*	*98.06*	*96.00*	*96.32*
Phosphorus:										
Soluble inorganic	62.39	69.29	53.39	58.99	90.00	91.60	89.26	89.70	73.76	77.39
Soluble organic	58.62	63.33	43.48	56.25	87.50	92.50	84.78	88.37	68.59	75.11
Total	*61.08*	*68.24*	*50.61*	*58.48*	*89.24*	*91.81*	*88.02*	*88.39*	*69.99*	*70.73*
Insoluble	....	....	....	....	....	....	....	....	....	....
Total	*70.32*	*77.50*	*61.97*	*69.00*	*92.13*	*93.78*	*90.78*	*91.44*	*78.80*	*83.09*

TABLE V—(*Continued*)

PROPORTIONAL DISTRIBUTION OF THE NUTRIENTS IN THE BROTHS AND DRIPPINGS DUE TO COOKING LEAN BEEF LOIN.

Description of sample	Boiled at 85° C. 3 hours.		Boiled at 100° C. 3 hours.		Roasted at 195° C. 1 hour.		Roasted at 100° C.	
							$1\frac{5}{6}$ hrs.	$2\frac{1}{3}$ hrs.
Laboratory No.	1966-67	1989	1968-77	1990	1978	1991	1979	1992
Time held in cold storage (days)	6	43	6	43	6	43	6	43
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
Water	38.40	31.91	41.95	41.76	30.06	23.47	22.20	19.55
Dry substance:								
Soluble	41.93	31.15	52.25	47.07	9.55	7.33	13.35	10.38
Insoluble	1.36	0.94	3.45	2.13	1.36	1.04	0.58	0.46
Total	*6.50*	*5.52*	*10.19*	*8.20*	*2.41*	*1.87*	*2.36*	*1.89*
Protein:								
Soluble coagulable	22.20	None	18.18	None	None	None	None	4.25
Soluble non-coagulable	68.60	45.24	54.55	58.93	48.15	24.44	34.48	46.36
Total	*59.09*	*45.24*	*49.35*	*58.93*	*33.33*	*24.44*	*27.14*	*23.86*
Insoluble	0.44	0.67	0.28	0.15	0.33	0.55	0.44	0.50
Total	*1.84*	*1.70*	*2.33*	*1.92*	*1.03*	*1.13*	*1.44*	*1.59*
Organic extractives:								
Nitrogenous	38.46	31.09	50.50	41.38	4.95	3.81	7.92	5.26
Non-nitrogenous	40.40	34.52	55.40	48.05	6.20	4.35	10.74	6.33
Total	*39.59*	*33.10*	*53.33*	*45.18*	*5.69*	*4.13*	*9.60*	*5.88*
Fat	3.62	1.58	11.50	3.59	3.75	2.20	0.79	0.38
Ash:								
Soluble	40.48	32.93	51.81	44.58	10.75	7.23	13.04	10.84
Insoluble	...	...	.....	...	..	...	....	....
Total	*34.69*	*27.27*	*43.88*	*38.14*	*9.92*	*6.90*	*12.00*	*8.82*
Nitrogen:								
As soluble protein	58.73	45.18	49.35	58.89	32.64	24.45	26.74	22.52
As soluble non-protein	38.25	30.81	50.77	41.78	4.44	4.20	7.77	5.41
Total soluble	*41.87*	*32.94*	*50.38*	*45.12*	*9.02*	*7.76*	*12.62*	*10.09*
Insoluble	0.43	0.66	0.29	0.14	0.35	0.53	0.48	0.52
Total	*5.40*	*5.02*	*7.11*	*6.33*	*1.37*	*1.43*	*2.06*	*1.94*
Phosphorus:								
Soluble inorganic	37.61	30.71	46.61	41.01	10.00	8.40	10.74	10.30
Soluble organic	41.38	36.67	56.52	43.75	12.50	7.50	15.22	11.63
Total	*38.92*	*31.76*	*49.39*	*41.52*	*10.76*	*8.19*	*11.98*	*10.61*
Insoluble	...	.....	....	...	....	...	....	....
Total	*29.68*	*22.50*	*38.03*	*30.34*	*7.87*	*6.22*	*9.22*	*8.50*

can be said regarding the soluble organic phosphorus, other than that the general tendency indicated a slight decrease in those obtained from the 43-day meat. Inasmuch as the soluble inorganic form is distinctly higher in the sample from the 43-day cold storage meat and the organic form is about the same, it is natural to expect the conditions which existed in regard to the total soluble phosphorus. Here, the differences in favor of the meat kept in storage for the longer period varied from 9.0 per cent. of the total amount in the 100° C. roast to 20.5 per cent. in the 100° C. boiled meat and gave an average of 12.7 per cent. for all the cooked samples. The percentage of insoluble phosphorus was higher in the case of the boiled meats obtained from the 43-day storage sample, averaging 31.7 per cent., but in the case of the roasted meats there was but little difference. Finally, the total phosphorus appears to have been more in abundance in the cooked meats from the samples which were held in cold storage for the longer period. In the case of the Aladdin 100° C. roast, the greater percentage amounted to only 3.0 per cent. of the total quantity, while in the 100° C. boiled meat, it reached as high as 23.5 per cent., and if the average of all four samples be considered, there was a total phosphorus content which was 11.8 per cent. greater than that of the 6-day cold storage sample.

The Proportional Distribution of the Nutrients in Cooked Meats.

Having considered in detail the nature of the cooked meats, calculated to the various forms, and also the broths and drippings, it will be instructive to study briefly the percentage distribution of the nutrients in each case, that is, assuming the sum of the constituents in each meat and its corresponding broth or dripping to be equivalent to the original uncooked sample, an approximation as to the differences in the nature or character of the two meats can be obtained by calculating the proportion of the various constituents in the uncooked and samples. In taking the sum of the respective constituents as being the equivalent of the uncooked meat, instead of using the direct analysis of the raw loin cut itself, a much better comparative set of data will be had throughout,

since it will be recalled that during the process of cooking, the percentage of coagulable, non-coagulable, soluble and insoluble protein, the corresponding forms of nitrogen and the soluble and insoluble dry substance were so altered that a proportional relation of these forms in the cooked and uncooked meats obtained directly would be meaningless for this comparison.

The data in Table V show the results expressed as above described, for the meats, broths and drippings. However, inasmuch as the statements which are to be made in regard to the meats apply in a reciprocal manner to the respective broths or drippings, the discussion will be confined to the first item alone.

First, it will be seen that on an average, the longer stored meats after cooking contained a greater percentage of their original moisture than did those which were kept for the shorter time, being 70.82 and 66.85 per cent. respectively. In the case of the 100° C. boiled meats, this difference was very slight, but in the other three cases, it was quite pronounced, varying from 2.65 per cent. in the 100° C. roast to 6.58 per cent. in the 195° C. roast. Further, the boiled meats showed that they retained approximately two-thirds of their water while the roast meats retained about three-fourths.

The forms of dry substances indicated several interesting facts. Of the total amount of the soluble form in the uncooked meats, the cooked samples from the 43-day storage meat held a larger percentage. The average of all the tests showed that the meats from the 6-day samples contained 70.74 per cent. and that those from the 43-day samples contained 75.25 per cent. of the total amounts in the respective uncooked samples, making a difference of 4.51 per cent. The maximum variation in the 85° C. boiled meats was 7.75 per cent., and the minimum variation in the 195° C. roast meats was 2.22 per cent. The insoluble dry substance showed but very slight differences in the proportional amounts, averaging 98.31 and 98.86 per cent. for the four tests from the 6- and 43-day meats. The total dry substance gave practically the same results as the insoluble form, showing that the meats from the 43-day storage sample contained 1.0 per cent. more of the total amount in the uncooked sample. Comparing the boiled and roasted meats, the proportional amounts of soluble, insoluble and total dry substance averaged 56.10, 93.03, and 92.39 per cent. for the former and 89.85, 99.14, and 97.87 per cent. for the latter.

In the case of the various proteins, the soluble coagulable form was noticeably higher in the samples from the 6-day stored meats, ranging from 100.0 per cent in the roasted meats to 77.80 per cent. in the 85° C. boiled meat. The samples from the 43-day stored meats showed that this form was apparently coagulated to a greater or less extent, during the process of cooking. In each case, except in the 100° C. roast, there was no soluble coagulable protein. The average of all tests showed that cooked samples from the meat kept for the shorter time still retained 89.9 per cent. of the original amounts, while those from the meats which were kept for 43 days still contained only 23.9 per cent. The non-coagulable protein showed that the cooked meats from the sample which was kept for the longer time, tended to lose less of their initial amount of this form than did the ones which were obtained from the meat stored for 6 days. The 100° C. boiled meats were an exception to this statement, but the average of all the tests indicated that samples from the 43-day stored meat contained 56.3 per cent. and that those from the 6-day sample contained 48.5 per cent. of the amounts in the respective uncooked meats. The same general statements which were just made in connection with the non-coagulable protein apply to the total soluble protein. The average of the soluble protein for all the respective experiments was 59.5 per cent. and 57.3 per cent. for the cooked meats from the 43- and 6-day samples. The insoluble protein showed but a very slight variation between any two of the cooking experiments. In fact, the differences were so small for the insoluble protein that it can be stated that the time of storage has no influence upon this constituent, the average being 99.63 per cent. for the cooked sample from the 6-day meat, and 99.53 per cent. for that from the 43-day meat, with a maximum difference of 0.23 in the 85° C. boiled meats, and a minimum one of 0.06 in the 100° C. roasted meats. Again, the proportion of total protein in the various cooked meats was practically the same in each of the four cases, being on an average for the samples stored for 6 days 98.34 per cent., and for those kept for 43 days 98.41 per cent.

The organic extractives indicated consistent variations throughout, which appeared to be due to the effect of the time of storage. In the case of the nitrogenous form, the boiled meats which were

procured from the 43-day uncooked samples contained on an average 8.20 per cent. more of these extractives than did those from the 6-day sample, while the corresponding roasted meats contained 1.9 per cent., making an average difference of 5.05 per cent. for all the cooked meats. The percentage of non-nitrogenous extractives in the cooked meats from the 43-day stored sample also indicated that these meats lost less during the process of cooking, averaging for those from the 43-day meat 76.69 per cent., and for those from the 6-day meat 71.81 per cent., making a difference of 4.88 per cent. The proportional amounts of the total extractives showed that the cooked meats from the samples which were kept for the longer time were the higher, averaging for all the tests a difference of 4.98 per cent. It is of interest to note at this point, again, the influence of the method of cooking upon the quantity of some of the constituents which were removed: in the boiled meats about 43 per cent. and in the roasted meats about 6.0 per cent. of the total amount of the extractives in the uncooked meats passed into the broths and drippings respectively. It will also be of special interest to note that the amount of crude fat was higher in each case for the samples from the 43-day storage meat, the greatest difference being in the 100° C. boiled sample 7.91 per cent. Averaging all the cooked meats for the 6-day sample showed that they lost in cooking 2.98 per cent. more of the fat than did those from the 43-day meat.

The soluble ash as well as the total ash both showed the same tendency as the fat, namely, to be higher in the meats from the 43-day sample. In the case of the soluble form, the greatest differences were in the boiled meats, being 7.55 per cent. in the 85° C. cooked meat, and the smallest ones were in the roast meats, being 2.20 per cent. in the case of the Aladdin 100° C. cooked meat. The average of all tests gave a difference of 5.12 per cent. in favor of the cooked samples from the 43-day storage meat. The total ash in the 85° C. boiled meat from the sample stored for 43 days, indicated that of the original amount in the uncooked meat, 72.73 per cent. was retained during the cooking, while in the case of the corresponding 6-day samples, the amount was 65.31 per cent., making a difference of 7.42 per cent. In the Aladdin roast, the same tendency seems to have been apparent but to a less extent, being 91.18 and 88.00 per cents. respectively for the samples from the 43- and 6-day meats, and showing a difference in favor of the former of 3.18 per cent. Averaging all the four tests, there was a variation of 5.06 per cent., showing that the samples from the longer stored meat lost less of their total ash content during the process of cooking than did those which were from the sample kept for the shorter period, 6 days.

The total soluble and total nitrogen indicated in the former case that the cooked meats obtained from the 43-day stored sample retained the greater percentage of the original amount in the uncooked meat: The 85° C. boiled meats showed the greatest difference in the total soluble form, being 8.93 per cent., and the 195° C. gas-roasted meats showed the smallest difference, 1.26 per cent., averaging for all the tests a gain of 4.52 per cent. The proportion of total nitrogen was about the same in each of the four tests with the samples from the 6- and 43-day stored meats. There was a slight tendency in favor of the sample from the longer stored meats, being in the maximum case, the 100° C. roast, 0.12 per cent. Averaging all tests, there was a difference of 0.32 per cent. It is noteworthy that the roast meats showed almost no influence due to the time of storage. The average of both roast meats gave 98.28 per cent. for the meats from the 6-day sample and 98.31 per cent. for those from the 43-day sample. In the case of the boiled meats, the differences are greater than for the roasted ones, yet not very large, considering that over 93.0 per cent. of the nitrogen was retained in the cooking. The average of the two boiled meats gave 93.72 per cent. for cooked meats from the 6-day sample and 94.32 per cent. for those from the 43-day sample, making a difference of 0.60 per cent.

The forms of phosphorus represented, the soluble inorganic, soluble organic, total soluble and total, all showed to a greater or less extent that the cooked meats from the 43-day stored sample retained more of these constituents during cooking than did the ones from the 6-day meat. The respective percentage averages were for the cooked meats from the 6- and 43-day samples 73.76 and 77.39 per cent. for the inorganic, 68.59 and 75.11 for the organic, 69.99 and 76.73 for the total soluble, and 78.80 and 83.09 for the total, making a difference in each instance of 3.63 per cent., 6.52 per cent., 6.74 per cent. and 4.29 per cent. As in the case of the total nitrogen, the boiled meats indicated the greater influence from storage. This fact was especially true with the inorganic and total soluble forms of the phosphorus.

SUMMARY.

Having now considered in detail the chemical composition of the cooked meats, both in per cent. of the fresh substance and the uncooked meats themselves, the nature of the losses and the proportional distribution of the various constituents in the cooked meats and the broth and drippings which resulted from the boiling and roasting of the samples of lean beef loin which had been held in cold storage for 6 and 43 days, the following summary shows the effect which seems, in these cases, to have been produced during the interval of 37 days of storage.

First, from the chemical examination of the cooked meats, obtained from the respective 6- and 43-day storage samples, the average data in each case show, when calculated to the fat-free basis and then to the same moisture content, that the cooked meats from the longer stored sample contained, when compared with those from the 6-day sample, 11.3 per cent. more of soluble dry substance, 41.6 per cent. less of coagulable soluble protein, practically the same percentage amount of total soluble protein, and 1.9 per cent. less of total protein; that the percentage of the nitrogenous and non-nitrogenous organic extractives were each 17.4 higher; that the ash content was about the same; that the percentage of total soluble nitrogen was 14.7 per cent. higher while that for the total nitrogen was but 0.5 per cent. lower; that the percentage of the soluble inorganic, the total soluble and the total phosphorus were respectively, 22.9, 11.1, and 10.5 per cent. higher and that the ratio of the soluble non-protein nitrogen to the total protein nitrogen was 1 : 12.3 for the samples from the 6-day meat and 1 : 10.5 for those from the 43-day meat.

Second, the composition of the cooked meats calculated in per cent. of the uncooked showed in general: that of the samples obtained from the 6- and 43-day stored meats, those from the latter lost 3.34 per cent. less during the process of cooking; they contained 2.24 per cent. more of water and hence were juicier; their soluble, insoluble, and total dry substance showed a percentage increase over the 6-day meat of 13.4, 2.5, and 3.7 per cent. respectively; the percentage of insoluble and total protein were practically the same as those in the 6-day samples; the nitrogenous, non-nitrogenous and total organic extractives were respectively 15.7, 15.3, and 15.5 per cent. greater; even after allowing for the differences in the broth and drippings, the fat showed an increase amounting to 8.4 per cent. of the total in the samples from the 6-day meat; the percentage of total ash was 7.0 per cent. greater; the soluble inorganic and the total soluble phosphorus showed percentage gains which were respectively 24.5 and 12.7 per cent. of the total amounts in the other samples; and the total soluble nitrogen was 16.9 per cent. higher, while the percentage of total nitrogen was about the same as in the meat from the 6-day sample.

Third, the proportional amounts of the various nutrients which were retained in the corresponding cooked samples from the 6- and 43-day cold storage meats, showed the following facts in regard to the samples which were from the meat that was kept in cold storage for the longer time: Of the total amounts of constituents found by summing the composition of the respective cooked meats and the corresponding broths and drippings, these meats retained on an average 3.97 per cent. more of water; 4.53 per cent. more of soluble dry substance; 5.05, 4.88, and 4.98 per cent. more of nitrogenous, non-nitrogenous, and total organic extractives respectively; 2.98 per cent. more of fat; 5.12 and 5.06 per cent. more of soluble and total ash; 3.63, 6.52, 6.74, and 4.29 per cent. more of soluble inorganic, soluble organic, total soluble and total phosphorus respectively. Further, these meats lost practically the same proportional amounts of the insoluble and the total forms of dry substance, protein and nitrogen as did those from the 6-day sample, being respectively for the cooked meats from the 43- and 6-day samples 98.86 and 98.31, 95.63 and 94.63, 99.53 and 99.63, 98.41 and 98.34, 99.54 and 99.61, and 96.32 and 96.00 per cent. In comparing the boiled and roasted meats, it was seen that in every case where there was any appreciable difference between the storage samples, the former cooked meats showed the effect to a greater degree.

Finally, it may be stated in general: That, many of the differences between cooked meats from the samples which were held in cold storage for 6 and 43 days, corresponded to those which were found to exist for the uncooked refrigerated samples.

That the cooked meats from the 43-day storage sample lost less in cooking either by boiling or roasting than did those from the 6-day sample, the broths and the drippings in these cases being on the average lower in their percentage content of soluble, insoluble, and total dry substance, of organic extractives, of soluble protein, of soluble ash, and of fat.

That the cooked meats from the longer stored sample were higher in their percentage content of moisture and were therefore juicier, higher in soluble and insoluble dry substance, in nitrogenous, non-nitrogenous and total organic extractives, in fat, in total ash, and in soluble inorganic, total soluble and total phosphorus. Further, the percentages of total nitrogen, insoluble and total protein were practically the same as were those for the samples from the 6-day storage meat. Therefore the cooked meats from the 43-day samples, judging from the chemical composition, were at least as nutritious as were those from the samples stored for the shorter period of time.

The authors wish to acknowledge the valuable assistance of Miss E. C. Sprague and Messrs. J. M. Barnhart and L. F. Shackell in connection with the analytical work.

URBANA, ILLINOIS,
April 3, 1909.

ADDRESSES.

PINE PRODUCTS FROM PINE WOODS.[1]

BY JOHN E. TEEPLE, PH.D.

The last year or two have been disastrous to the industry of recovering pine products from pine wood in America. For more than five years the Savannah price of turpentine had not fallen below fifty cents per gallon, and had been steadily strengthening each year, not fluctuating greatly, rising a little in winter and falling a little in summer as the new crop came into the market. In 1907 the price for a time exceeded seventy cents per gallon at Savannah. These apparently firm conditions of the market for so long a time encouraged all sorts of experiments and ventures in turpentine recovery. The records of the patent office for these years reflect the general confidence in the future of the industry, in the form of scores of patents on possible and impossible processes and apparatus for the extraction of turpentine, rosin and other products from pine wood.

Plants multiplied throughout the South, at costs varying from \$3,000 or \$4,000 up to \$100,000 or more. The total number of such plants of all descriptions must have been nearly 100. The number in actual operation to-day is probably less than 10, and very few of these claim to be financially successful at the present price of turpentine.

From seventy cents or more per gallon the price of turpentine declined steadily during 1907 to about 50 cents at the end of the year, and to 35 cents after the middle of 1908; since then it has been below 40 cents most of the time. Almost any type of plant could operate successfully at 75 cents per gallon; nearly every one is a source of regret at 40 cents per gallon.

Three different woods have been used as raw materials of the industry, *viz.*, the long leaf pine (*Pinus palustris*) in North Carolina, South Carolina, Georgia, Florida, Alabama, Mississippi, Louisiana and Texas; the Norway pine or red pine in Michigan, Minnesota and the Province of Ontario; and the Douglas fir in Washington, Oregon and British Columbia. In any one of the three cases the raw material may be especially selected resinous wood, or it may be sawmill refuse.

Saw-mill Refuse.—This consists of slabs, edgings and sawdust. (The amount of refuse varies much with the size of logs, sizes of lumber cut, and kind of saws.) The slabs and edgings are passed through an edging grinder or chipper and cut into chips of about the size used in making paper pulp. The total of chips and sawdust is not far from 200 cubic feet per 1000 feet of lumber sawed. As a cord of wood when reduced to chips of uniform size occupies 200 cubic feet or over we may say that a sawmill cutting 100,000 feet of lumber a day will have the equivalent of nearly 100 cords refuse or waste material. In most sawmills the sawdust furnishes sufficient fuel and the other refuse is burned. A large number of patents have been granted on processes and apparatus for the destructive distillation of this waste material, in the form of chips or sawdust. So far as the writer knows no one of them has ever reached the stage of actual manufacture, because sawdust and chips are such poor conductors of heat that more or less complicated mixing devices are necessary to accomplish the distillation and the yields obtained do not warrant the expense of installation and repairs. The only method of treating sawmill waste on a manufacturing basis has been steam distillation.

The chips or sawdust or both are brought by conveyors to storage bins, from which they are dropped into retorts. These retorts are usually cylindrical affairs made of boiler iron and have 200-500 cubic feet capacity. If set horizontally a helicoid screw conveyor or other device is used for discharging the chips after the treatment. If set vertically the bottom is arranged as a door to drop or slide away and allow the chips to fall, sometimes with the aid of shakers operated by hand. Where only sawdust is used there is no difficulty in discharging a large vertical retort through an 18-inch or two-foot hole in the bottom. Another type of retort is a cylindrical or spherical one hung on trunnions.

Whatever the shape of the retorts, they are provided with steam pipes perforated for the admission of live steam, and distributed throughout the retort in such manner as the designer thinks will give most complete extraction of turpentine from the chips. The retort being filled, live steam is turned on for one-half hour to one hour in the case of sawdust and for one to two hours in the case of chips. This extracts most of the turpentine and some of the pine oil. Distillation and rectification with steam separate the product into wood spirit of turpentine and pine oil, the only two products obtained from mill waste. Quite a number of recovery plants of this type have been built particularly in Florida, but careful inquiry seems to show only one in actual operation at the present time. This is one designed by the writer for a sawmill in Florida. The other ones have apparently met their fate from fire, low price of turpentine, financial considerations, or faults in construction which made it necessary to use labor in handling the refuse wood at some stage of the process. The amount of wood to be handled is so large and the yield of turpentine so small, comparatively, that hand labor must be reduced to a minimum or the plant cannot operate.

[1] Presented to the Seventh International Congress of Applied Chemistry, 1909.

The yields obtained from sawmill waste are subject to many fluctuations. Where all the timber has been boxed for turpentine before being cut for lumber the slabs are very rich and the yield is uniformly good. There seems to be a regularity in the changing yield, however, probably depending in part on the season at which the logs are cut, and in part on imperfect condensation in summer. During the winter months a yield of about one and one-half gallons refined product to 100 cu. ft. chips or sawdust is the rule. In summer, particularly in July and August, it may fall to one-half that amount or less.

Since the raw material costs nothing we have to consider only the daily labor and expense charges, and interest, insurance, depreciation and taxes. The daily labor and expense charges usually lie between ten and twenty cents per gallon in a properly constructed plant, depending of course on the yield. The average cost including all charges should lie between twenty and thirty cents per gallon in a sawmill cutting at least 100,000 ft. per day. A plant should hardly be installed in connection with a smaller mill.

One other form of utilizing sawmill waste may be mentioned. A plant has been operating in Texas in which shavings from a planing mill were converted into paper pulp, from which a very good grade of brown paper was made. In the preliminary digestion a small amount of turpentine is recovered.

As far as I know mill waste from the long leaf pine is the only kind whose recovery has been attempted commercially in this country.

Light Wood.—By far the most important raw material in the pine products industry is the light wood, a name given to the non-decaying resinous parts of the dead long leaf pine trees. The formation of this material and the general development of the industry have been traced in another place.[1] We have to deal here only with the present condition of the plants. This light wood is found wherever long leaf pine grows in the eight southern states mentioned above. The largest quantities and best quality are found in turpentine orchards that have been worked for many years and finally abandoned. If boxed trees have afterward been cut for timber the stumps are very rich down to three or four inches below the level of the ground. Exclusive of short stumps about one or two cords of light wood may usually be obtained per acre. The light wood is usually cut into four-foot lengths for convenience in handling, but in one plant at least it was the custom to bring in whole logs 8–16 feet in length and feed them directly into the edging grinder.

Hand labor is used exclusively in cutting and preparing the light wood. The wood from stumps is no different from ordinary light wood, excepting that it averages a little richer in turpentine and is more expensive to prepare for the plant. At some plants stumps are sawed off near the ground level, then split by hand. At others a charge of dynamite was placed in the tap root just below the ground level. This splits the stumps so that very little further labor is required. A third method is to use the stump puller, but in this case the wood must be split by hand and carefully freed from stones and gravel, before it goes to the edging grinder. Prepared in any of these ways great care must be used in the selection of the light wood going to the plant. A cord of light wood may yield anywhere from 6–30 gallons of turpentine. The men who are working with it regularly become very expert in judging its quality, and as the cost of good light wood is not greatly in excess of that for poor wood this skill becomes a valuable asset. For good light wood, yielding an average of 15 gallons turpentine per cord we may consider $2.50 per cord a minimum and $4.50 per cord a maximum price delivered at the plant.

Given good lightwood at the plant there are three general methods of dealing with it, *viz.*, steam distillation use of a bath, and destructive distillation. These will be considered separately.

Steam Distillation.—More plants of this type than of any other have been constructed during the last five or six years. The simplicity of the process and the large amount of turpentine that could be made in a day were its recommendations. The plants consist essentially of an edging grinder to reduce the light wood to chips, storage bins and retorts like those discussed under the sawmill waste, conveyors to handle fresh and extracted chips, boilers, engines, condensers and refining stills and tanks. The chipped wood is placed in the retorts and treated with live steam for from three to twelve hours. With good condensing capacity the chips are sufficiently exhausted in four hours. Five or six plants were constructed to use superheated steam but the advantage of this, if any, was so small that all early abandoned its use.

There has been wide divergence in practice as to the steam pressure used in extracting the chips, some running at 5–10 pounds, others much higher. One ran at 100 pounds, pressure or over. There is no doubt that the high pressure extracts more pine oil if it is continued, since the temperature in the retort is nearer the boiling point of the oil. The best results, however, are obtained by varying the pressure from nothing to about 20 pounds two or three times during the digestion; this forces the steam to penetrate the chips and on releasing the pressure each time a mixture of steam with spirit and oil is forced out of the chips, supposedly following the law governing the distillation of two immiscible liquids. Operated in this way the temperature in the retort does not vary appreciably from 100° C. It remains only to separate the large amount of water from the small amount of oil, either at the condenser or in a large separating tank, and to purify the oil by distillation. An addition of soda ash or lime is often made to the crude oil in order to neutralize any acids. Other additions of oxidizing or reducing agents to improve the odor are not uncommon, but it is doubtful if they have any real value The final products are wood spirit of turpentine and pine oil. If properly separated the turpentine has a sp. gr. of about 0.865 and conforms with all the tests for gum turpentine, as usually applied except that the fraction distilling above 165° C. is a little larger, due to the presence of some pine oil. This and its characteristic odor of freshly cut pine are the only real distinguishing characteristics. In a commercial way a large number of varnish manufacturers and other turpentine users have assured me that it could be used under all circumstances to replace gum spirit of turpentine without detection were it not for the characteristic odor. This refers only to a properly refined sample; of course one which was incompletely separated from pine oil would not dry as rapidly as it should and might be otherwise objectionable.

[1] *J. Soc Chem Ind.*, **26**, 811 (1907)

The pine oil is a white or light yellow liquid of specific gravity about 0.940 and boiling for the most part between 205° and 220° C. It has been more fully described elsewhere.[1]

In various degrees of purity it now finds a very considerable market; some especially pure forms are being exploited for their medicinal value.

These two are the only products of steam distillation plants. The yield on fairly good wood will average 14–16 gallons crude oil per cord, about 10 per cent. of this being pine oil.

In one plant using 60–80 cords per day of uniformly selected wood a record for one month showed an average for the whole period of 15 1/2 gallons per cord, while on only one day of the month did it fall below 14 gallons. This shows at once the strength and weakness of the system. With turpentine at 50 cents per gallon or above the large output and uniformity of operation makes it a good investment. At present prices they operate at a loss. It is rumored that one steam plant is still operating in Georgia, but I have been unable to verify the rumor. The future of steam distillation, if it has one, lies in some form of utilization of the extracted chips, which at present are only used as fuel. Two steam plants have been built in Ontario to distil Norway pine. One has closed on account of low prices and the other never started to operate.

Rosin Bath Process.—The idea of using a bath in the retort was patented about 45 years ago, but the present plants are under what are known as the Weed & Pope and Davis patents and are comparatively recent; four plants in all have been constructed, two in N. C., one in Ga. and one in S. C. Two plants are now operating, one in North Carolina and one in Georgia. In the North Carolina plant the wood is cut into 4-foot lengths, placed on cars and run into steel retorts. When the retorts are closed hot rosin is pumped in until the wood is covered. The bath is kept at about 195° C. for nearly 10 hours. A continuous circulation of the rosin bath over a fire keeps the temperature constant. The temperature alone is sufficient to drive out nearly all the turpentine and by the aid of live steam a considerable amount of pine oil is driven over as well. When the extraction is finished the rosin bath is pumped off, and the extracted wood sold for fire wood or for destructive distillation. The rosin bath is found to increase in volume, due to the extraction of some rosin from the wood, and from time to time a portion is sold as A. B. C. rosin. The other products, turpentine and pine oil, are similar to those obtained by steam distillation. This process has the advantage over steam distillation that a part of the initial cost of the wood is covered by the sale of extracted wood, and further that the yield of pine oil is larger. It has the disadvantage that a much larger investment is required to produce the same amount of turpentine per day.

The plant operating in Georgia begins with a bath of high-boiling hydrocarbon in place of the rosin bath. Since there is a continual increase in the bath, due to the extraction of rosin from the wood, it seems probable that it would be essentially a rosin bath after a few months' use. In this plant each charge is treated eight hours.

Destructive Distillation.—Destructive distillation for the recovery of tar was the first method of utilizing light wood. It has persisted to the present time and with low-priced turpentine is probably as satisfactory as any other method. There are certainly more destructive distillation plants in operation now than any other type. The products they sell are so numerous and so subject to change under varying market conditions that it is difficult to outline any uniform process. The matter is further complicated from the fact that each plant has its own products, trade names and standards carefully arranged to disagree with those of other plants. In a general way we may say that the light wood is always used in four-foot lengths, and is not as carefully selected as in other types of plants. The retorts are cylindrical, placed horizontally, and open at one or both ends. No cars are used like those in hard wood distilling plants, excepting in a one-retort plant in Georgia. All labor is by hand. The retorts are from 3/4-cord to 5-cord capacity, usually between one and two cords; charcoal or ordinary cordwood furnishes the heat; this is sometimes increased by burning the gas escaping from the retorts. A charge requires from 24 hours to 48 hours for completion. In some retorts of large diameter it may be extended to five days. Attempts are usually made to arrange the flues so that the retort will be heated to a uniform temperature throughout, but the results in this respect are seldom satisfactory. The turpentine and other more volatile liquids come over during the early part of distillation. They are placed in a copper still, neutralized with alkali and distilled, yielding first a low-boiling liquid of 0.840 to 0.850 sp. gr. having a very sharp disagreeable odor. This ultimately finds its use in some one of the many disinfectants. The next product up to about 0.865 sp. gr. constitutes wood spirit of turpentine. This can be properly refined to a material equivalent to spirits made by the steam or rosin bath methods, but the mixture from which it comes is so much more complicated that this is seldom done. The wood distiller finds it more profitable to market his wood spirits as an inferior grade at a lower price without further refining. The work of the office of wood utilization of the Government forest service is at present directed toward this question of refining destructively distilled spirits.

After 0.865 sp. gr. it is customary to take off a second grade of wood spirits probably consisting essentially of dipentene with some sylvestrene. After this again comes a mixture of the last two products with the terpineol-like constituents of pine oil mentioned above. The sp. gr. of this fraction may go as high as 0.930. It has an agreeable odor and finds its use among essential oil and disinfectant manufacturers. There remains in the still a soluble combination of cresol-like bodies with alkali. This serves as a basis for a soluble disinfectant. The heavier distillates from the retort are sold as wood creosote oil, wood preserver (supposed to be one-half creosote oil and one-half neutral oil), paint oil, oil of tar, cable coating, insecticides and disinfectants, including considerable quantities of sheep dip. With the exception of oil of tar, there is little uniformity in the products from the different plants or in their methods of preparation. In most cases the methods are supposed to be secret and include liberal uses of lime, potassium nitrate, litharge, alkalies and alkaline carbonates. The oil or tar has a fairly steady market; for the others each plant must make a market for its own products.

An outlet at the bottom of the retort serves for the escape of tar. This is known as retort tar, and is usually darker

[1] *J. Am. Chem. Soc.*, **30**, 412 (1908).

in color and lower in price than kiln tar. If great care is taken during the distillation so that the tar is removed as fast as formed and so that there is no excess heat, then the tar may be obtained as light in color as kiln tar.

The other products include charcoal, about 40–50 bushels per cord of wood. This is used as fuel in the plant or is sold in local markets. Pyroligneous acid is equivalent to about 26 pounds glacial acetic acid per cord. This is a very weak solution and is either sold as such, or thrown away or converted into black iron liquor. It is not at present converted into acetate of lime in any of the plants. Wood alcohol has been recovered in two or three plants but was given up as impracticable. The yield was about one gallon per cord. While the destructive distilling plants apparently have the best opportunity for success with low-priced turpentine on account of the variety of products they can make even they are not optimistic. No one of them so far as I can find claims to be operating at a profit under present conditions.

Other Methods.—A number of other methods, mainly extraction with various solvents, have been tried, but it is too soon to report of their value. One plant in Michigan, working on Norway pine, first steams the chipped wood, then extracts with petroleum distillate of about 60° Bé., using vacuum to recover the solvent. The yields so far have been about 15 gallons crude oil and 250 pounds rosin per cord, much less than is usually claimed for the process. Spirit of turpentine, made either by the steam process or by the rosin bath, has become a definite article of commerce commanding a price fairly uniform in its relation to gum spirits of turpentine. In fact the differences between the product and gum spirits are of such a minor character that it is reasonable to suppose they will soon disappear entirely, in part from more uniformity in refining wood spirits and in part from a gradual passing away of a still firm unfounded prejudice against anything masquerading as turpentine excepting gum spirit of turpentine made by the old process.

As to the future of the industry all depends on the price of turpentine. At present prices it is not probable that any plants so far constructed can operate profitably, excepting those utilizing mill waste where the raw material costs nothing or nearly nothing.

At 40 cents and above for spirits of turpentine the bath processes claim they can operate without loss.

Excepting in rare instances most steam distilling plants will remain closed when the price is below 50 cents per gallon.

In the case of plants for destructive distillation so many factors enter into the question of their successful operation that it is impossible to make any general statement. Some claim to be operating now with very little or no loss, while others were forced to close when turpentine was 60 or 70 cents per gallon.

The many other methods suggested have still to demonstrate at what level they can live.

New York, March, 1909.

NOTES AND CORRESPONDENCE.

ON INDUSTRIAL FELLOWSHIPS.

In accordance with the invitation of the editor of This Journal, I append a statement of a scheme of Industrial Fellowships which was initiated by me in an article entitled "Temporary Industrial Fellowships," in the *North American Review* for May, 1907, and which appeared subsequently as the last chapter in a book intended to draw the attention of American manufacturers to the applicability of modern science to industrial operations ("The Chemistry of Commerce," *Harper's*). During the last two years this scheme has undergone a somewhat notable development not only in the number and value of the fellowships established, but, as well, in the increased advantages which I have found it practicable to obtain from the donating corporations in behalf of the university. It should be plainly stated, however, that the scheme is as yet inevitably experimental and tentative and that each individual fellowship must always, from the very nature of the case, be an experiment. It is not pretended either that the scheme in its details has reached its ultimate development; all that can be said is that during the past two years it has shown no sign of weakness on the part of any one of its constituent factors but has, on the contrary, grown constantly stronger.

Before entering into the details of the scheme itself, it may be of interest to state here the fundamental considerations upon which it was based. In advancing them there is no thought of attempting to speak dogmatically; they are simply personal convictions which account for the scheme.

(1) It is not the function of a professor of industrial chemistry *in a university* to establish courses and laboratories for undergraduates who propose to become chemists, and for the following reasons: Current industrial practice is always ahead of text-book presentation and laboratories of industrial chemistry having apparatus and processes in miniature are for the most part puerile in their resultant teachings and convey to the student an exaggerated impression of his utility to the factory to which he subsequently goes. Worse than all is the fact that in taking such courses the chemical undergraduate is deprived of just so much pure chemistry, *i. e.*, real chemistry. The university insists that the chemical undergraduate shall undertake cultural and cognate studies. The result is that in taking industrial chemistry he must omit a particularly good course in physical chemistry or he must remain with half a year in organic rather than with a full year, or he must squeeze his training in combined qualitative and quantitative analysis within a year or a year and a half. If the university does not insist upon cultural studies the resultant "Chemist" might as well be called a cook for any claim he may have to recognition as an educated man. The foregoing considerations do not apply to trade schools or to technical schools. The function of a university is to free men to the exercises of their maximum powers; in a trade school the young man enters already limited.

(2) Speaking with whatever truth there may be in generalities, the condition of American manufacture with respect to progressive and correct factory practice and with respect to genuine efficiency is seriously bad. (I am referring not to the mechanical but to the chemical phase of manufacture.) The necessity for this progress and efficiency in the past two or three decades has been marked by certain factors. These appear to have been a wealth of raw material everywhere at hand, an excessive tariff that concealed from the manufacture the practical presence of his problems, a certain facility possessed by the American

manufacture for what may not unfairly be called business intrigue, which enabled him to supplement the waste in his factory by combinations for the elimination of competition, and, finally, the needs of a rapidly expanding population which would swallow anything. Two years ago, however, conditions were rapidly changing. The unexampled and wasteful production of the country was bidding fair to result in overproduction; in the practice of business intrigue no manufacturer had anything to learn from another; the wealth of raw material had in a large measure been aggregated into the holdings of a few men who would release them only at an onerous and distressful rate; the tariff, high as it was, was unable to exclude many articles made under scientific supervision, and the tariff, itself, lay and lies in increasingly unstable equilibrium. These facts convinced me that American manufacture was approaching a crisis and that there would soon be a realization that safety in manufacture could be gained only through efficiency. I may say here, that this conviction has been amply substantiated during the last two years. Few men have any idea of the ever-increasing anxiety of American manufacture to secure factory efficiency. It may safely be predicted that during the next five years the supply of research chemists will be wholly inadequate to the demand; it is, indeed, to-day.

(3) The American manufacturer has neither the knowledge nor the experience requisite for the establishment of successful scientific research.

(1) He does not know what problems he has, nor their relative importance.

(2) He does not know what kind of knowledge is required to solve these problems.

(3) He does not know how to go about it in order to obtain the men who are really expert in the different kinds of knowledge requisite to the solution of these problems.

(4) He does not know how to judge the qualifications of training and creative power among the different men available; he frequently, for example, chooses an analyst when a synthetic man is required and *vice versa*.

(5) He does not know how to estimate a proper expenditure for laboratory space and supplies and library facilities which these men will require on the basis of the least money for the largest efficiency.

(6) He does not know how to coördinate the work of these men with the factory operations.

(7) He does not know how to coordinate the work of the researchers on his staff, one with another, so that they will be mutually helpful one to another.

(8) He does not know how properly to estimate the progress made by these men so that he may know when he is getting real efficiency.

(9) He does not know how to systematize the work of his scientific staff so that it will work automatically.

(10) He does not know how to treat a man of science in his factory in giving him either power or trust.

This last consideration is responsible for much of the failure of American factory research. The condition of the research chemist in the American factory is often actually pitiful and may be compared to that of cultured governors in a home of codfish aristocracy.

Whatever the foregoing generalities may be worth, and they are, of course, merely personal convictions, they are, taken together, responsible for a scheme by which in a spirit of sympathetic coöperation the university and the manufacturer might each profit—and the public through both—a scheme of Industrial Fellowships. This scheme in its present development is perhaps best exploited by presenting here one of the later fellowships; for example, Fellowship No. 7. It will be understood that the fellowships differ one from another, owing to the particular conditions relating to each and owing, occasionally, to the idiosyncrasies of the donor.

Fellowship No. 7.—For the purpose of promoting the increase of useful knowledge, the University of Kansas accepts from the A. B. C. Glass Company, having head offices at New York, the foundation of a temporary industrial fellowship to be known as the A. B. C. Fellowship.

It is mutually understood and agreed that the conditions governing this fellowship shall be as follows:

The exclusive purpose of this fellowship is an investigation into the optical properties of glass in relation to its chemical constitution to the furtherance of which the holder shall give his whole time and attention, with the exception of three hours a week which he shall give to work of instruction in the chemical department.

The fellow shall be appointed by the chancellor of the university, the director of the chemical department and the professor of industrial chemistry; he shall have made previously a reputation in research; he shall be a member of the university, and shall pay all regular fees with the exception of fees for laboratory and supplies, for which his instruction shall be taken in lieu, unless in the opinion of the appointers his demands become excessive, in which case the donor shall be expected to reimburse the university; he shall work under the advice and direction of the professor of industrial chemistry; and he shall forward, periodically, through the professor of industrial chemistry, reports of the progress of his work to the A. B. C. Company.

For the support of this fellowship, which shall extend through a period of two years from the date of appointment of the fellow, the A. B. C. Glass Company agrees to pay fifteen hundred dollars ($1500) per year, payable annually, to the university on the date on which the fellow begins work at the university. This sum shall be paid by the university in monthly instalments to the holder of the fellowship.

Any and all discoveries made by the fellow during the tensure of this fellowship shall become the property of the A. B. C. Glass Company, subject, however, to the payment by them to the fellow of ten (10) per cent. of the net profits, to be commuted at the desire of either party through the arbitration provided for herein, arising from such discoveries, it being understood that the fellow shall be regarded as the inventor. At any time during the tensure of his fellowship the holder shall, at the option of the donor, take out patents at the expense of the donor on condition that at the time of making application therefor he shall assign his right to the donor under the conditions of this agreement. At or before the expiration of the fellowship, the business services of the fellow may be secured by the A. B. C. Glass Company for a term of three years on condition that the terms of such services are satisfactory to both parties at interest.

In the event of any disagreement between the donor and holder of this fellowship, it is understood and agreed that the chancellor of the university, or one whom he may appoint,

shall act as arbiter as to all matters of fact, that his decisions shall be binding upon the parties at issue, and that they shall obtain such decision before having recourse to the courts.

It is also understood and agreed that during the tensure of this fellowship the holder may publish such results of his investigation as do not, in the opinion of the company, injure its interests, and that on the expiration of the fellowship the holder thereof shall have completed a comprehensive monograph on the subject of his research, containing both what he and others have been able to discover. A copy of the monograph shall be forwarded to the A. B. C. Company, and a copy shall be signed and placed in the archives of the university until the expiration of three years from that date, when the university shall be at liberty to publish it for the use and benefit of the people.

Signed on behalf of the University of Kansas.

Date................

Signed on behalf of the A. B. C. Glass Company.

Date................

A careful reading of the above agreement, or perhaps it had better be called, memorandum, may make apparent certain relations (1) to the university; (2) to the manufacturer; (3) to the fellow; (4) to the public; (5) to the professor of industrial chemistry.

(1) (*a*) The university gains increased opportunities of fulfilling its function in promoting research. (The fact that the research has directly useful ends in view does not make it necessarily any the less scientific or valuable.) (*b*) It obtains three hours a week of gratuitous instruction from men particularly well qualified from the standpoint of ability, knowledge, and enthusiasm to give it. (*c*) The chemical department of the university obtains the catalytic influence of these men.

(2) (*a*) The manufacturer obtains the advantages of enormously increased laboratory facilities. (*b*) He obtains the advantage of adequate library facilities—a most important advantage, the lack of which has seriously hampered much factory research. (*c*) He obtains consultive advantages, for the fellow appointed is at liberty to go with direct or hypothetical questions to specialists in the different fields of chemistry or to specialists in other fields of scientific knowledge, such as biology, physiology, physics, etc. This has also turned out to be an important advantage. (*d*) He obtains a complete freedom from supervisional responsibility over this work. (*e*) He obtains on the termination of the fellowship the services of a man educated to his particular needs.

(3) The fellow obtains all the foregoing advantages (*a–b–c*) ascribed to the manufacturer, and in addition he obtains (*d*) the all-important sympathetic coöperation of the manufacturer together with the (*e*) inside knowledge of the factory processes, and (*f*) the university's environment sympathetic to research, and (*g*) a freedom from all petty interferences and jealousies of shop people, and the pot-shot judgments of factory officials. Finally, if he proves worthy of it, he obtains a position for which he has become, through his training, peculiarly qualified.

(4) Since at the end of three years all work done under any fellowship must be published free to the public, the public thus obtains new implements of civilization. It must be remembered that it is only through the industries that any useful discovery can go to the people.

(5) Since this whole scheme depends upon sympathetic coöperation it can only be carried out through a professor of industrial chemistry who regards it as a sacred trust. It is, therefore, necessary, positively necessary that the professor of industrial chemistry should, so far as any material sense is concerned, gain absolutely *nothing*, otherwise his donors would not trust him with the details of their secret processes, nor would his fellows trust him with their progress.

There have been so far accepted by the university the following fellowships:

(1) An Investigation into the Chemistry of Laundering, having for its object an improvement which will save in some measure laundered fabrics. It yields $500 a year, together with 10 per cent. of the net profits.

(2) A Search for a New Diastase. The present source of the best diastase is expensive. The investigation has as a matter of fact developed into an attempt to make a new fodder upon scientific principles. It yields $500 a year and, under the original agreement, 10 per cent. of the gross proceeds for three years.

(3) An Attempt to Utilize the Constituents of Waste Buttermilk, which, at present, in butter factories goes down the drains. These constituents, which it is desirable to conserve, are primarily caseine, and secondarily, lactic acid and sugar of milk. The fellowship yields $500 a year and 10 per cent. of the net profits.

(4) An Investigation into the Chemistry of Baking. This investigation was established by the National Association of Master Bakers, with the object not only of improving the chemistry of bread, but, as well, of providing for the association a trained expert upon whom they could afterwards rely. It yields $500 a year, together with a lump sum to be settled by arbitration, if necessary.

(5) An Investigation into the Constituents of Crude Petroleum. I cannot with propriety state the precise object of this investigation. The fellowship yields $1,000 a year, and 10 per cent. of the net profits.

(6) An Attempt to Improve the Enamel upon the Enamel-lined Steel Tanks used in all kinds of chemical operations on a large scale. This fellowship was established by the largest manufacturer of these tanks in the world. It yields $1,300 a year, together with an additional consideration to be decided upon, for the service rendered by the chancellor of the university or one whom he may appoint.

(7) An Investigation into the Relation between the Optical Properties of Glass and Its Chemical Constitution. This fellowship yields $1,500 a year and 10 per cent. of the net profits.

(8) The Discovery of New Utilities for Portland Cement and of Improvements in Its Manufacture. This fellowship yields $1,500 a year and a large additional consideration dependent upon success.

The fellows for additional Fellowships Nos. 7 and 8 have not yet been selected. In addition to the foregoing fellowships there are certain others assured but not yet established.

(9) An Investigation into Certain Glands of Deep-sea

Mammals. It yields $1,500 a year and an additional consideration to be decided upon by arbitration. This fellowship is to be a benefaction.

(10) The Discovery of New Utilities for Ozone. It yields $2,000 a year and 10 per cent. of the net profits.

The tensure of all fellowships is two years.

It is regrettable that in accordance with the terms of the agreement, it is impossible to publish at this time the results so far obtained. It may be said, however, that the progress of the fellows has been gratifying. It is significant in this connection that Fellowship No. 1, which expires shortly, is to be continued at double the value for three months, at the end of which time the donors will either take the fellow and his process into the factory or they will continue his fellowship through a third year at the increased amount, while with Fellowship No. 2 the donors have already indicated their intention to continue it throughout a third year; the progress of the others has exceeded that of the first two and has surpassed expectations.

Most of these fellowships have arisen through letters of inquiry from the various companies. I have not gone out seeking fellowships in general. Had I done so it is not unreasonable to suppose that by this time there might have been from thirty to fifty. Owing to the fact that these fellowships have no relation to ordinary fellowships and that the scheme is essentially a new one, it has been deemed advisable to establish them at intervals. Proceeding in this way, and learning as one went, the scheme has undergone a natural and advantageous development. The degree to which it has been systematized, its effect upon the chemical department, the results of the relations of the different researches and researchers to one another, and the wholly unexpected interactional relation of the donating companies to one another I shall reserve for a future communication. While it should be said that as yet this scheme of Industrial Fellowships is wholly experimental and tentative, it ought also to be said that the two years' experience has not shown that it is any other than a sane and practical relation between the university and industry to the advantage of all concerned. ROBERT KENNEDY DUNCAN.

UNIVERSITY OF KANSAS,
May 12, 1909.

AN ACCURATE AND RAPID MEASURING DEVICE.

In the routine work of these laboratories, it is necessary, daily, to fill a large number of vials or other small containers, with antitoxin solutions. This system of measurement is commonly performed by the use of a graduated burette, with the usual ground-glass stop-cock at the lower end. The trouble with the use of the burette for this performance consists in the fact that such doses must necessarily be drawn by unskilled assistants, with the result that the reading of the burette is not taken so sharply as when employed by a trained chemist in the analytical laboratory.

For a long time we observed the variations of average employees with the use of the burette in the standard way. From our own experience with this class of laboratory help and apparatus, together with the data from other serum laboratories, we have found that the maximum error in the measurement of a 3 cc. dose of antitoxin was, in some cases, as great as 6/10 cc. or 20 per cent.

Knowing the personal variation with the use of the old style burette, one must either include this in his calculation or risk a short or excessive dose, as the case may be. It was our aim to invent an automatic burette which could be set by a lever or screw, to deliver a given quantity of a solution and when so adjusted, could not fail to deliver *only* that quantity, without any careful meniscus reading on the part of the operator.

We have succeeded in perfecting the apparatus shown by accompanying diagrams. This automatic burette has advantages over the old style straight tube in regard to both accuracy and speed, with the opportunity to vary the volume delivered with considerable range.

Fig. 1.

The principle depends upon a ground piston of glass or metal, moving freely but closely, within a ground glass barrel. The solution is allowed to enter and empty by slight pressure, through a four-way stop-cock. The volume delivered is exactly that amount displaced by the movement of the plunger from the point of the adjusting screw, to the opposite end of the barrel. It will readily be observed in the diagram that the volume of solution pushed forward and out at any time must, of necessity, be equivalent to that which flows in behind the plunger and occupies the space just vacated and which is represented by one complete movement of plunger from the point of

the adjusting screw to the opposite end of barrel, going in either direction. Since the volume of each delivery is determined by the distance traversed hy the moving piston, it must follow that all deliveries from a given adjustment are exactly the same.

By weighing successive deliveries of this burette, it is found to be thoroughly practical to employ it for a continuous use, with an error of less than 1/200 of 1 per cent.

All argument about reading of meniscus has been avoided. There is no question in the mind of the operator, at the completion, in regard to the "initial reading," which sometimes arises with work by the old style burette.

By employing this machine in our serum laboratories, an employee can fill from 400 to 600 doses of antitoxin per hour, with sterile precautions throughout.

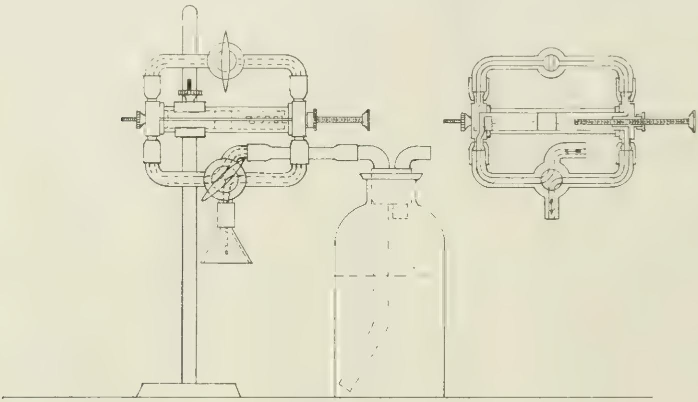

Fig. 2.

We have found it of even greater advantage to us for filling broth, gelatine, agar, or other culture media into test-tubes where we require both a reasonable degree of accuracy and maximum speed.

This device will deliver accurately from 1000 to 2000 measurements of less than 10 cc. in a single hour.

It may be employed to advantage for the measurement of drug solutions, where each volume taken is a therapeutic dose, and also in the chemical laboratory where accuracy and speed are requirements.

It is so constructed that it may be made completely of glass and platinum, which makes it possible to employ it for the measurement of strongly acid and alkaline solutions.

Isaac F. Harris, S. D. Beard.
Lederle Antitoxin Laboratories,
New York.

[From the Department of Dairy Husbandry of the University of Wisconsin.]

THE DETERMINATION OF FAT IN CHEESE BY THE BABCOCK TEST.[1]

The directions for operating this test given in text-books, read as follows. "About 15 cc. of warm water are added to the cheese in the test bottle and this is shaken occasionally until the cheese softens and forms a creamy emulsion with the water. A few cc. of acid will aid in this mixing and disintegration, the process being hastened by placing the bottles in tepid water. When all lumps of cheese have disappeared in the liquid, the full amount of acid is added and the test completed in the ordinary manner."[1]

Having many samples of green cheese and curd to analyze daily for fat, it became necessary to find a way to dissolve the curds quickly, so that the work could be finished in a reasonable time. It was found impossible to dissolve the samples by shaking the bottles, prepared as directed above, for an hour or more, even when kept in hot water, although this method works well enough with old cheese. Instead of trying to disintegrate the curd by application of external heat, it was found more satisfactory to soften the curd to a pasty condition, at the much greater temperature attained, when 17.6 cc. of sulphuric acid were added to 10 cc. of hot water in the bottle with the sample. In the pasty condition, the largest lumps of curd are instantly shattered by vigorous shaking, and dissolved. No attempt is made to break up the curd before adding the acid. The whole operation takes about the same length of time as required in the analysis of cream by the Babcock method. There is no danger of loss, if care is used to add small portions of acid, at first.

The heat generated, when the acid runs down the side of the test bottle, is much less than when the two layers of acid and water are shaken together, later. To avoid loss by boiling over, it is necessary that the first portions of acid added should be small, and be well mixed with the water, by shaking, before adding more. In this way the boiling point of the acid and water mixture is raised more rapidly than the temperature of the bottle contents. Using water at 70° C., the temperature finally attained in the bottle is about 120° C. The directions are as follows: Weigh 8 to 10 grams of cheese or curd into a Babcock test cream bottle. Add 10 cc. of water at 65–70° C., and without delay add 17.6 cc. of sulphuric acid, in small (1 cc.) portions at first, mixing the acid and water by shaking, after each addition. When the acid is all in, the final vigorous shaking shatters the pasty curd lumps to fine grains, which dissolve quickly in the strong acid, without further heating.

J. L. Sammis.

DETERMINATION OF CARBON BISULPHIDE IN BENZOL.

The determination of carbon bisulphide in benzol is one which presents serious difficulties, owing to the volatility of the

[1] Published by permission of the Director of the Wisconsin Experiment Station.

[1] "Testing Milk and Its Products," Farrington and Woll, 1908, p. 96. See also "Modern Methods of Testing Milk and Its Products," L. L. Van Slyke, 1907, p. 84.

substances under examination, and their comparative stability towards ordinary reagents. Moreover, the compounds formed from carbon bisulphide are difficult to purify and readily decompose. The most accurate method for this determination is by the pressure tube, estimating total sulphur as in the ordinary ultimate organic analysis. A very excellent modification of this method is published by Holland and Phillips.[1] This method, however, involves heating under pressure, and can be entrusted only to a very experienced operator.

Therefore, an easier and quicker, but nevertheless accurate, method was sought after. Nickels[2] precipitates the carbon bisulphide from the benzol by a solution of caustic potash in absolute alcohol, filters the precipitate of xanthate of potash, and after transposing this to the copper salt, weighs the latter. This method was tried. It was found that copper xanthate partly decomposed on drying at 100° C.; moreover, some potassium xanthate remained dissolved in the alcoholic potash benzol mixture and finally, the precipitate of potassium xanthate retained some potassium hydrate which could not be removed by washing. These several errors combined in such a manner as to give consistently low results. It might be interesting to note in this connection, that in one trial where the copper xanthate was ignited to copper oxide, at the first, a very strong garlic odor was noted, afterward identified as ethyl xanthic ester. The probable reaction is

$$Cu(SCSOC_2H_5)_2 = CuS + COS + CS\begin{cases} OC_2H_5 \\ SC_2H_5 \end{cases}.$$

Potassium xanthate seems to be the best compound by means of which we can fix carbon bisulphide in a definite form. It is quite stable in alkaline solutions, but cannot be purified from alkali in a quantitative way. In acid solutions, it is decomposed with reformation of carbon bisulphide. It was, therefore, determined to convert the carbon bisulphide in the benzol into potassium xanthate and then to try oxidation by bromine in alkaline solution, changing the sulphur of the bisulphide to sulphuric acid and determining the latter as the barium salt. This method proved successful. It gives close results and can be carried out in apparatus such as would be found in any ordinary commercial laboratory. The details of handling the method, as selected by many experiments, follow:

Weigh about 2.5 grams of benzol in a weighing-bottle of 50 cc. capacity and add 2.5 cubic centimeters of a saturated solution of caustic potash in absolute alcohol. Allow to stand 5 minutes stoppered, then fit with the return cooler, and warm to about 60° C. for 1 hour. Now remove the condenser and wash everything into a large beaker (1500 cc.). The water solution now contains the carbon bisulphide as xanthate of potash; the unchanged benzol is also mixed with it. This latter is removed by heating on a steam bath for a few minutes. The solution is then made strongly alkaline with caustic potash and an excess of bromine water added. The mixture is warmed on a steam bath. Sulphur is sometimes precipitated at once, but this is later redissolved by the action of the bromine. The solution should be heated and bromine water added until oxidation is complete. The solution will then be perfectly clear and have a slight yellow color. At no time should the solution be allowed to become acid before oxidation is complete. Then the liquor is acidified and the excess of bromine (and there should be an excess) is boiled off and the sulphuric acid determined by barium chloride in the usual way. The proportion is

$$\underset{466}{2BaSO_4} : \underset{76}{CS_2} = \text{weight } BaSO_4 : X.$$

Some results follow:

Per cent. CS_2 in benzol tested.	Per cent. found.
4.95	4.75
4.95	4.85
4.95	4.80
5.05	4.95
4.66	4.60

In conclusion would say that although the results are a little low, due probably to loss of CS_2 in adding the alcoholic potash, yet they come well within the limits of experimental error. The operation can be carried on without any special apparatus and is sufficiently accurate for all commercial requirements.

JOHN MORRIS WEISS.

BARRETT MFG. CO. LABORATORY,
CHEMICAL DEPT., FRANKFORD, PA.

[1] *Jour. Soc. Chem. Ind.*, **1884**, p. 296.

[2] *Chem. News*, **43**, 148–250.

TWO CONVENIENT DEVICES FOR USE IN THE MICROSCOPIC STUDY OF OPAQUE OBJECTS.

The steadily increasing use of the vertically illuminated microscope for the study of metals, alloys, ores, cements, paint, fluxes, etc., has given rise to several sources of illumination ranging from the simple Welsbach burner and a bull's-eye condenser to an arc lamp with its cooling cells and long optical train. Some are very expensive and occupy a large amount of space, others are inadequate, and the majority are more or less difficult to regulate.

The following apparatus occupies but little space, is regulated with ease, and can be built by any instrument-maker or machinist at a very small cost.

The device (Fig. 1) consists of a telescope tube which has a maximum extension of ten inches and is mounted in a trunion provided with a set screw so as to permit the tube as a whole to be tilted at any angle. A vertical adjustment is provided for by means of a rack and pinion movement.

In the back of the telescope tube is mounted a bull's-eye condenser having a focus of two (2) inches, and at the front of the tube is a plano-convex lens whose focal length is one and three eighths (1 3/8) inches.

The rear of the telescope tube carries a shield on the bottom of which is fastened a slot in which any desired color screen may be placed. Fastened to the shield also is a stiff brass rod on which there is a movable carrier for an acetylene jet. This carrier consists of two (2) pieces of brass tubing brazed together at right angles to each other, and each of which is provided with a set screw so that the source of light may be moved up or down, forward or back, or turned and set in any position and at any angle with reference to the plane of the rear lens, a method of mounting which permits the use of any portion or all of the flame from the thinnest edge to the fullest width.

The jet is connected by means of rubber tubing with any

form of generator. The one here shown is of the "Drip" type and is provided with a catch bottle which experience has shown to be desirable.

The microscope is provided with a Bausch & Lomb vertical illuminator having a plain glass reflector which reflects light coming to it through an aperture in the side of the mounting down through the objective upon the object, from which it is reflected through the microscope to

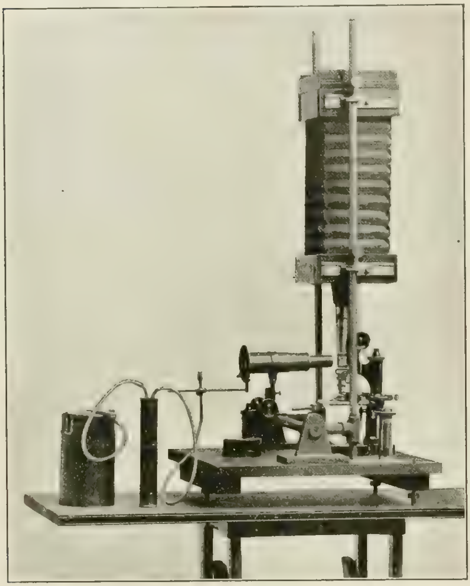

Fig. 2.—An illuminator.

the eye. Below the illuminator is a "Quick-acting Nose Piece" which permits of a ready change of objectives without any change of alignment and which experience has shown to be preferable to a "revolving nose-piece." The top of the tube is so arranged that it slips readily into a light-tight connecting tube carrying on the camera.

The length of the tube from the eye-piece to the nose-piece is 160 mm.

Many of us have had more or less trouble in leveling irregularly shaped samples for use under the microscope, such as a section of a flange, a broken cement briquette, an ore specimen or other similar material.

To meet these conditions, the following device (Fig. 2) will be found useful. This consists of two pieces of brass tubing of any convenient diameter (the one here figured is 4 in. wide x 6 in. high) which telescope, and are ground to fit. The outer tube carries a strip of any convenient size across its top and securely fastened to it. This strip is centrally tapped to receive a screw carrying 20 threads to the inch. This screw has a milled head and is about an inch longer than the tube. This adjustment screw is fastened to the inner tube by means of a screw bottomed in it in such a manner that the inner tube can be readily raised or lowered but does not revolve. The inner tube should be of a height sufficient to give a good bearing and not to be thrown off of level; in the apparatus here figured, it is two and a half inches in height. The whole is set up on a base plate provided with a groove which receives the outer tube and which carries two-hinged clamps screwed into the plate and provided with set screws to lock into the tube when in position.

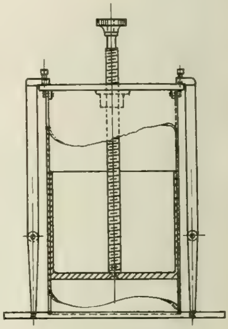

Fig. 2.—A leveling device.

The method of use is as follows: A lump of modeling clay is stuck on any slide suitable for the purpose. The specimen is now set up in the proper position on the wax. The slide is placed on the base plate, the tube set over it and clamped down, and the specimen leveled perfectly by turning the milled head of the adjusting screw so as to bring the inner tube (which must, as a mechanical necessity, travel evenly) down on the specimen and forcing it into the wax, thus giving a serviceable mount and assuring a level surface for examination under the microscope. The set screws are now released, the clamps thrown back, the tube lifted and the specimen is leveled and mounted ready for study.

WIRT TASSIN.

SOLUBLE ARSENIC IN MIXTURES OF LEAD ARSENATE AND LIME SULFUR SOLUTION.

The mixing of lead arsenate with lime sulphur in a combined spray has been advocated and used with success by the Department of Entomology of the Oregon Station. The possibility, however, of injury resulting from the use of this combination, due to the formation of soluble arsenic, has led this department to investigate the amounts of soluble arsenic formed on combining these insecticides under varying conditions.

Commercial lead arsenates are ordinarily very slightly soluble in water. The New Jersey Station reports from 0.15 per cent. to 0.77 per cent. soluble arsenic oxide in samples examined by them.[1] The moist arsenates as examined by us have run from 0.13 per cent. to 0.42 per cent. soluble arsenic oxide.

The method usually employed in determining soluble arsenic in lead arsenates is that suggested by Haywood, of the U. S. Bureau of Chemistry, in which the sample is allowed to stand in contact with distilled water for ten days, with occasional shaking. This is an extreme test and the New Jersey Station shorten the time of contact to twenty-

[1] *Bull.* **214**.

four hours. Some comparative tests with the latter method were made by us with results as follows:

Distilled water, 24 hours	0.28% sol. As_2O_5
Tap water, 3 hours' constant shaking	0.11% " "

Agitating with tap water for three hours was thought to more nearly approach actual field conditions.

In determining the soluble arsenic formed on mixing lime sulphur and lead arsenate, lime sulphur solution of 1.30 sp. gr. (34° Baumé) was diluted 1 : 10 and the moist lead arsenate, triturated free from lumps, was added in the proportion of 2 1/2 lbs. to 50 gallons of lime sulphur solution. The mixture was agitated three hours in a shaking machine, and an aliquot of the solution analyzed for arsenic by oxidizing with hydrogen peroxide, according to the method of Avery, running down with sulphuric acid, rendering alkaline with bicarbonate and titrating with iodine, as in the modified Gooch and Browning method.[1]

To test the method, known quantities of arsenic were added to a lime sulphur solution analyzed as above with the following results:

(1)	As_2O_5 added	0.00143 gram
	As_2O_5 found	0.00132 "
(2)	As_2O_5 added	0.00258 "
	As_2O_5 found	0.00250 "
(3)	As_2O_5 added	0.01490 "
	As_2O_5 found	0.01490 "

The mixture of lime sulphur and lead arsenate darkens slightly, owing to the formation of small quantities of sulphide of lead.

In some dozen analyses, made of the mixture, the soluble arsenic oxide varied from 0.28 per cent. to 0.43 per cent., showing the amount of arsenic dissolved by the lime sulphur to be very small and approximating that dissolved by water alone. Grasselli lead arsenate and Niagara lime sulphur were used in the majority of the tests. An addition of slight excess of caustic soda to the lime sulphur increased the amount of soluble arsenic some threefold in the one test that was made.

Gillett[2] found that 1 lb. of As_2O_5 in 1200 gallons of water or approximately 1 part of As_2O_5 to 10,000 parts of water exerted slight injury on foliage. 0.43 per cent. soluble arsenic oxide in a mixture containing 2 1/2 lbs. of lead arsenate to 50 gallons is equivalent to about 1 part soluble arsenic oxide in 37,000 parts of water.

Our results would then seem to indicate that in so far as excessive amounts of soluble arsenic being formed is concerned there is no danger in mixing lead arsenate and ordinary lime sulphur according to above-mentioned conditions.

A further study of the reactions involved in the mixture as well as the solubility of lead arsenate under varying conditions is being made in this department.

C. E. BRADLEY.

OREGON EXPERIMENT STATION,
CHEMICAL LABORATORY,
CORVALLIS, OREGON.

MANGANESE IN STEEL.

The writer takes this opportunity to add a few remarks to his discussion of the sources of error in Volhard's method.[3]

He has found since, that in high-carbon steels, the carbon does interfere in the scheme he there ultimately lays down. This is shown in the following results:

	.40c	1.30c	60c	1.20c	1.00c	.57c
Evaporated and baked	0.49	0.67	0.96	0.22	0.47	0.95
Not evaporated and baked	0.52	0.75	0.99	0.26	0.53	0.99

Therefore, the process now is: 3.3 grams are dissolved in nitric acid in a porcelain dish, evaporated and baked to decomposition of nitrates, taken up with strong hydrochloric acid, cooled, transferred to a 16 oz. Erlenmeyer flask, marked at 500 cc., slowly, while keeping cold, neutralized with zinc oxide (commercial) emulsion to stiffening, diluted nearly to mark and shaken, allowed to stand to settle, enough to see that liquid is colorless, a teaspoonful of solid zinc oxide added and well shaken, diluted to mark, and when settled, 250 cc. clear liquid decanted off, transferred to 16 oz. Erlenmeyer, diluted, boiled, and titrated with permanganate of strength 0.0056 cc., permanganate divided by 10 is per cent. manganese. A blank is made on 60 cc. permanganate reduced with hydrochloric acid.

GEORGE AUCHY.

NEW BOOKS.

This list was prepared by Mr. Paul Escher, 1319 Pearl Street, Alameda, Cal.

Metallurgy, Geology.

Ueber Die Entwickelung u. Bedeutung der Kartelle in der Deutschen Eisenindustrie. By E. ALTMANN. 8°, 100 S. m. Tab., Diss. Darmstadt, 1908.

Ueber Einige Chrom- und Mangan-Legierungen. By G. HINDRICHS. 8°, 40 S. m. 7 Fig. u. 9 Tab. Diss., Gottingen, 1908.

Experimentelle Untersuchung des Thomasprozesses. By L. LAVAL. Halle a/S. 1909. Mk. 5.

Ueber Einige Eisen-Silicium-Kohlenstoff Legierungen. By W. GONTERMANN. 8°, 45 S. m. 9 Fig., 6 Tab. u. 1 Taf. Diss., Gottingen, 1908.

Neue Methode Zur Massanalytischen Bestimmung von Mangan, Eisen u. Chrom. (**Sammlg. Berg- u. Hüttenmännischer Abhdlgn. Heft 33**). By E. LUCHMANN. Kattowitz, 1909. Mk. 2.

Der Gegenwartige Stand der Nickelgewinnung mit Besonderer Berucksichtigung der Betriebe Bei Frankenstein in Schlesien. (Sammig. Berg- u. Hüttenmännischer Abhdlgn. Heft 32). By A. RZEHULK. Kattowitz, 1909. Mk. 2.50.

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[1] *Bulletin* **107**, Bureau of Chemistry, p. 39.
[2] *Iowa Bull.*, No. 2.
[3] *Journal Am. Chem. Soc.*, **18**, No. 6.

Emailleindustrie. Europas, Adressbuch samtl, europ. Stanz- u. Emaillier werke m. genauer Bezeichnung der Erzeugnisse, des Betriebsumfanges, der Produktionfähigkeit, etc., eingeteilt in Gruppen der einzelnen Länder. Bezugsquellenliste f. die Fabrikate der Stanz- u. Emaillierwerke, landerweise geordnet. Bezugsquellenliste f. alle in der Emailleindustrie benötigtens Machinen, Werkzeuge, Materialien, etc. 8°, IV, 255 S. Dresden, 1909. Mk. Kart 6-.

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SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN CHEMICAL SOCIETY, DETROIT MEETING.

The Fortieth General Meeting of the American Chemical Society was held at Detroit, Michigan, by invitation of the Society of Detroit Chemists, from Tuesday, June 29, to Friday, July 2, 1909, with an attendance of over three hundred. Dr. F. T. F. Stephenson, president of the Society of Detroit Chemists, welcomed the members and visitors at the first general session held at the Central High School, on Tuesday morning. Dr. W. R. Whitney, president of the Society, responded. He emphasized the great importance of getting acquainted at the general meetings of the Society. We could read the papers, he said, which were presented at the meetings in printed form and under more favorable conditions, but only at the meetings could we arrive at an appreciation of the personality behind the paper. Then we were in a position to say after reading a paper, "I can accept all that this man says at its face value because I know him;" or "I will discount this paper twenty-five per cent., I know the author." After Dr. Whitney's response, Secretary Parsons made the official announcements for the meeting in his usual vigorous and clear style, after which the various Divisions met in their appointed places. Of the Divisions, the Division of Industrial Chemists and Chemical Engineers easily led in point of attendance and number of papers read. Since the formation of this Division, the chairman, Dr. Little, of Boston, and secretary, Mr. Hyde, of New York, have spared no efforts to make of it an unusual success with most gratifying results. There was need for a closer affiliation of the industrial chemists and engineers in the Society, and they have joined hands with their officers to make the meetings pleasurable and profitable beyond the dreams of the organizers. A special report of the meeting of the Division will be found below.

New Chemical Laboratory, University of Michigan

In the evening, a theater party for ladies was arranged at the time the men were entertained at a smoker given by the members of the Local Committee. Both were successful. The smoker was characterized by the best of good fellowship, and the perfection of arrangements by the Local Committee made the event one to be long remembered with pleasure.

On Wednesday morning, the Divisions met again at the Central High School. After the recess for lunch, the members, ladies and visitors boarded special cars for the plant of Parke, Davis & Co. After a photograph of the party was taken in front of the offices of the company, groups were formed and guides escorted them through the works. All were impressed by the great variety of operations performed, the painstaking exactness everywhere observed and the high character of the employees. The bacteriological laboratories appeared to be especially worthy of praise. Dinner was served in the company's lunch room and in the evening there was a moonlight excursion from the docks in front of the plant up the Detroit River and into Lake St. Clair. There were music, dancing and refreshments, and all made merry and had a good time.

On Thursday morning, members and guests left on a special train for Ann Arbor, on invitation of the Regents of the University of Michigan, to be their guests for the day. At 10 o'clock a general meeting was held. President Angell, of the University, welcomed the Society and President Whitney responded. During the morning, the following addresses were heard:

H. E. Howe (for Industrial Division): Optical and Quartz Glass; Their Chemical and Physical Properties.

Alexander Smith (for Section of Chemical Education): The Place of Chemistry in the American College.

At the noon recess, a lunch was served the Society by courtesy of the Regents of the University.

The afternoon session was devoted to the Section of Chemical Education, the following papers being read:

S. Lawrence Bigelow: Some Ideals, Some Difficulties, and a Compromise for a First Course in Chemistry.

Arthur John Hopkins: A First College Course in Chemistry.

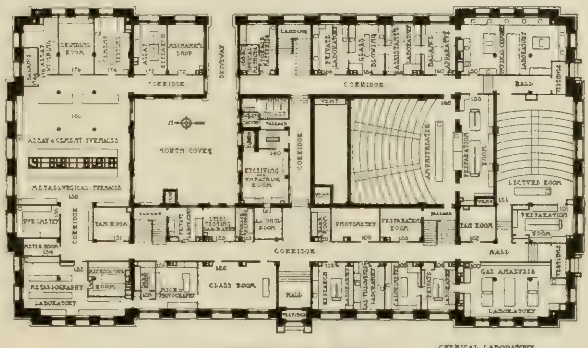
Lauder W. Jones: College Chemistry beyond the Elementary Course.

Harry McCormack: Laboratory Instruction in Industrial Chemistry.

Norman A. Dubois: Teaching by the Lecture System.

The great interest of those present, in the general subject, was shown by the lively discussion which followed the reading of the papers.

The University of Michigan is to be congratulated on its past and present splendid interest in chemistry and on the able men it has numbered on its chemical faculty. At present, is being erected on the campus, a magnificent chemical laboratory, at a cost of $250,000.00, which will be completed in the autumn of this year. The accompanying cuts show the general plan of the structure. When completed, it will take its place among the largest and best-equipped laboratory buildings in America.



+ FIRST + FLOOR + PLAN + CHEMICAL LABORATORY UNIVERSITY OF MICHIGAN

On Thursday evening, after the return from Ann Arbor to Detroit, the subscription dinner was held at the Hotel Ponchartrain, and was attended by about two hundred members and guests.

On Friday morning, provision was made for adjourned meetings of the Sections and Divisions, and the rest of the day was given over to excursions to various manufacturing establishments as follows:

Acme Lead & Color Works. Paints, White Lead by new process.

Detroit Salt Co. Rock Salt Mine, 800 feet deep.

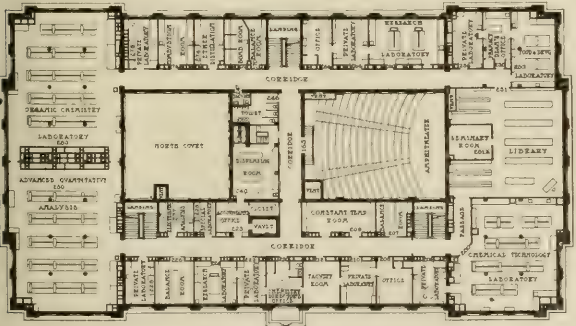
Goebel Brewing Co. Annual capacity, 350,000 barrels.

Hiram Walker & Sons. Distillery of "Canadian Club."

Hoskins Mfg. Co. Pyrometers and Electric Furnaces.

Berry Brothers. Varnish Manufacturers.

Among the most interesting plants visited was that of the Hoskins Manufacturing Co., where a special exhibit of electric furnaces was prepared.



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The three types of Hoskins furnaces in different forms and standard sizes were shown in actual operation. A complete connected train of apparatus, including Hoskins' combustion tube furnace run on standard voltage, for determination of the carbon content of steel, was displayed. A crucible furnace of standard voltage type, in connection with a Hoskins pyrometer, was shown in use for obtaining the "recalescent" points of steel specimens. Crucible and tube furnaces of heavy wire, low-voltage type, were shown in operation at a temperature of 1200° C. (2192° F.). These furnaces were controlled by small step-down transformers operating from the standard voltage circuit. Under working conditions of melting special nickel alloys, to be used in the production of resistance wire, the Hoskins type FC furnace was shown. This furnace produces temperatures as high as 2000° C. (3632° F.) by means of a carbon plate resistance unit worked at low voltage.

In connection with these furnaces, a complete installation of pyrometers was exhibited. Included in this was shown an illuminated dial meter, connected through a selective switch with several thermo-couples placed in the various furnaces on display. By moving the switch, instant indication of the temperature of any of the furnaces was shown on the meter. Separate instruments, including the well-known portable pyrometer, were also shown.

Of particular interest were the new type laboratory hot plates exhibited. These were in two styles, those with uniform heat distribution, and those with the heating unit were located in the center of the plate, both producing temperatures up to 350° C. (662° F.).

An inspection followed of the manufacture of these products. This included the resistance-wire producton department, the shops, assembling departments, and testing laboratories. Eighty members of the Society visited the plant. It was a general expression on their part that the electric heat production devices and exact temperature measuring instruments inspected, had an increasingly important bearing upon all branches of chemical work.

The Detroit Salt Company, with its rock salt mine 800 feet deep, into the salt strata underlying the city of Detroit, and the distillery of Hiram Walker and Sons, at Walkerville, were largely patronized by visitors.

On Friday night, members and guests left Detroit for their homes, and closed the most successful Summer Meeting the Society has ever held.

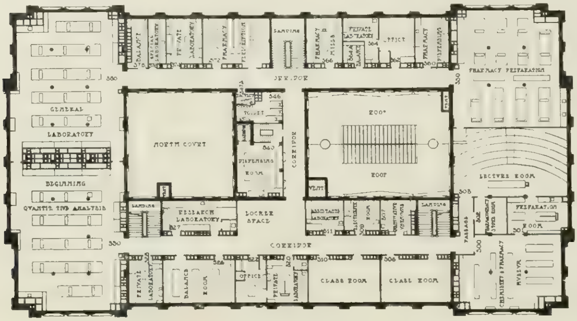
Next Winter's Meeting will be held at Boston, Mass., December 28 to January 1, in connection with the meeting of the American Association for the Advancement of Science.

THE DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS OF THE AMERICAN CHEMICAL SOCIETY.

TUESDAY, JUNE 29, 1909.

MORNING SESSION.

The meeting was called to order by the chairman, Dr. A. D. Little, who spoke briefly regarding the number of important papers to be read by the members and visitors.



THIRD FLOOR PLAN — CHEMICAL LABORATORY UNIVERSITY OF MICHIGAN

Owing to the very large list of papers to be read, there being 44 in all, the Chairman allotted the time of 15 minutes for the reading and discussion of each paper, except the reading of papers for which provision had previously been made.

The first business before the meeting was the reading of the minutes of the previous meeting, which were read by the Secretary, Mr. T. B. B. Hyde, and upon motion duly seconded and carried, accepted.

Dr. Little stated that there were a few changes in the By-laws at the last meeting which were submitted to Council, but as there were only two members of the committee having this matter in charge present, it was impossible to make a report at this time.

The secretary stated that he had no particular report to make, but said that the enrollment, as far as could be determined, not having the list with him, was about 800 members. This, he said, showed that the work done thus far, applied to all sections of the country, and not alone in this country, but to outside countries, and that if our work is to be made more interesting and effective, it must be done with this continued coöperation of the members.

Dr. Little stated that he knew of a club where every member was acquainted with all the other members, and that he felt that such acquaintance brought about better results and coöperation of the members, also that it was his desire to encourage coöperation and support in this Division, and in furtherance of same, asked each member present rise and give his full name, college, and a brief history of his work for the benefit of the others. Dr. Little then proceeded to give an account of himself and his work, being followed by the Secretary and members. This proved one of the best features of the meeting.

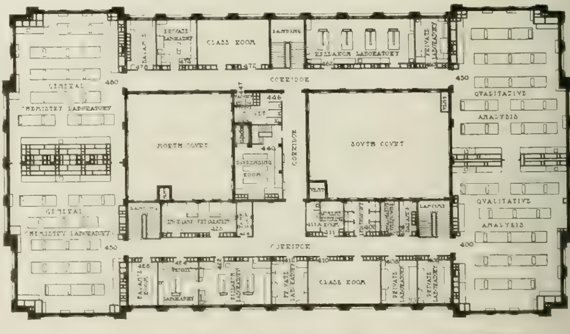
After the general introduction of members, Mr. Little asked Mr. W. M. Corse to give a short history of the American Brass Founders Association.

By Mr. Corse.

"I might say that the American Brass Founders' Ass'n., is an educational organization organized three years ago along the lines of the American Foundrymens' Association. The American Foundrymens' Association, as possibly you know, is an organization in this country which furthers the educational side of the cast iron and steel industries. The organization is probably eleven or twelve years old, and has done a good deal of educational work in the study of foundry work, more particularly on the iron end.

The American Brass Founders' Association publish a volume containing papers read at our conventions, etc., all of which are of interest to those in the iron and steel industries. The American Brass Founders' Association is allied with the American Foundrymens' Association, and has exactly the same objects in view with the exception that it deals in brass and non-ferrous metals instead of cast iron and ferrous metals. We had a meeting in Cincinnati, last month and appointed a committee to complete standard methods for brass and non-ferrous alloys to coöperate with the allied industries.

As Dr. Whitney was unable to be present at that meeting, I was delegated to represent this section. At that time we had present Dr. Hiller of the United States Geological Survey, who was there two days and gave a number of very



FOURTH FLOOR PLAN — CHEMICAL LABORATORY UNIVERSITY OF MICHIGAN

valuable suggestions along the lines of making samples. We are endeavoring this year to introduce, through the Bureau of Standards, two standard samples of brass. We intend to do the same thing for brass that the U. S. is doing for iron, and we have secured the coöperation of the United States Bureau of Standards in this work. Dr. Little was kind enough to suggest that a standing committee be appointed to cooperate from this Division. Dr. Little can

tell you better than I, the necessity to-day for the close coöperation of the theoretical man and the practical man who is operating the shop. It is one of the most difficult things, as you know, to smooth down the differences between the chemist and the practical man. Practical men will not come to a meeting like this because they have not enough interest in it. Therefore, if our members can get to work in conjunction with such an association as ours, we ought to accomplish a great deal in industrial progress.

The chemistry of brass is very little known, and you will find it pretty difficult problem to get definite information on it. The work of the Brass Founders' Association is to be the development of methods and standards which can be referred to by any man who wishes to make an analysis of brass, regularly or occasionally. There are probably not over fifteen men in the U. S. connected with brass foundry work directly.

The point I wish to make here is that the American Brass Founders' Association, being a trade organization, can coöperate with the American Chemical Society and get some very valuable information from the Society, and on that account, I should be very glad to offer my services in any way, in this work of coöperating, and wish to call this Division's attention to the fact that I have with me one of our members, Mr. Elliott, who will say a word to you along this line. Mr. Elliott is a practical brass man."

By Mr. Elliott.

"The brass foundry is one of the many departments of our business, and it presents more problems to our chemical department than all the others. If any of you go into the brass business and try to hunt up the authorities on brass,

you will find very few. You will find about one authority. He was a Mr. Brannt, who wrote a book about fifty years or more ago. The brass foundrymen are very much in the dark. They have no idea as to exactly how much lead, copper, zinc, tin, etc., is in brass and bronze, and very little idea how much heat these metals should receive in the foundry. Under or overheating will ruin them very quickly. They are ruined from different causes. None of them have

been standardized, and every man who goes into the brass business has to do his own pioneer work, so if the brass-foundry man comes into closer contact with the chemist, he will be lifted up into possibilities which he never dreamed of before.

As to my work, my particular line is the relation of brass, as well as the ferrous metals, to steam. We manufacture steam specialties, and this is a field which has not been investigated at all, thoroughly.

If any of you are inclined to research work, and have the time and capital, you cannot find a broader field, a more interesting, or one which will do more good for the foundry trade, than that of the brass foundry business."

The reading of the papers before the Section was then begun. The discussions following the papers were illuminating and instructive.

Mr Little adjourned the meeting at 1 P.M. to reconvene in the afternoon at 2.30.

AFTERNOON SESSION

Mr. Little called the meeting to order, opening with a few remarks upon the very enthusiastic attitude of all those present towards the work of the Division and outlining its possibilities.

There were present 109 members. The afternoon was spent in reading papers, and there appeared to be a more open and general discussion of them.

An adjournment was taken until the following morning.

WEDNESDAY, JUNE 30, 1909.

MORNING SESSION.

A continuation of the reading of papers showed much

original work, and in more than one instance the authors found that some part of their investigations had been paralleled, the resultant discussion proving of profit to those immediately interested.

In order to take advantage of the entertainment provided for the Society by Parke, Davis & Co., the meeting

was adjourned early, to be called to order for the remaining papers, Friday morning, July 2nd.

FRIDAY, JULY 2, 1909.

FINAL SESSION.

Upon the completion of the program, Mr. Little invited all present to join in an experience meeting. This proved most valuable and entertaining and brought home to the members more than ever the absolute need of coöperation by a free and mutual exchange of experiences, both in theory and actual practice to the several industries represented. Mr. Little said in part:

"If we take our proper place, we must regard the making of analyses and we do reading and writing. We want to get all the information we can. I do not mean that just because certain analyses are of the physical class that they are not as important as those made in the laboratory. I think we should be inclined a great deal more to engineering. The mechanical engineer has taken chemistry much to himself, and why should not the mechanical chemist test and determine the proper conditions of combustion and proper application of coal. This should be recognized as directly within the province of the chemist. Owing to the delicacy and infrequency of many of our methods, we are apt to think, perhaps, that the results we secure are of a higher order and more valuable than some results that the practical man gets quickly, and I think we should know more of the practical man and what the man on the job knows.

I remember a case where some shovels for a large electric railroad were sent in to us to determine which was the best shovel. Our client did not care about an analysis of the shovels, but wanted to know which would last the longest. Naturally, the first thing we thought of was an analysis. I happened to know the president of the Shovel Manufacturers' Association, and asked him the quickest way to determine which was the strongest shovel and which would wear the longest. He took the two shovels and striking one against the other, made a long gash in one, and handing me the one which was not damaged by the blow, stated it was the better shovel. This is just an illustration of the practical man *versus* the chemist, and the plan on which I am trying to work. The great majority of our business is on the contract basis where we undertake to look out for the interest of our clients at so much per year or month, and in order to carry out their requirements and look out for their interests, we must get quick and practical results. For instance, in order to tell whether a piece of cardboard is only one piece or is a multiplied board, the practical man takes the card and sets fire to it with a match at the corner, and as it burns the card separates into as many layers or piles as it may be composed of. If it is a 5-ply card, you get five separate layers.

If pulp paper contains sulphite, the best experiment to determine this is to take a clean dime and draw it across the paper. If this leaves a black streak on the paper then you know it is sulphite."

Mr. Little also gave a demonstration from a rough drawing with chalk, of a practical method of testing heat in large piles of coal by an auger. This auger has the lower portion drilled out and is filled with a maximum thermometer, and a man goes over the pile taking the temperature at any desired depth by simply boring into the coal to any desired depth up to 30 feet, the auger being provided with a sectional shaft. In this manner a man can make numerous tests of the coal in a day and determine at what depth in the pile the heat is the greatest. Sometimes a pile of coal is hottest about three feet below the surface.

Mr. Little further stated that he is in need of and anxious to find some young man with a good chemical training who knows something about library methods. He stated that he had been trying all sorts of records for keeping analytical data, and had finally adopted a large card system (size of cards about 6 x 8 inches), the cards having squares

on the back in which to note the data relating to samples, and lines on the front for the signature of clients when accepting the analysis.

Dr. Whitney stated that a half inch 6-strand copper wire hung up in the Torrid Zone would not stand, and that each strand showed that it had been broken sharply across. He further demonstrated this on the blackboard, making a diagram showing a six-strand cable with a jute core. When you

break open a strand, you find cracks in each wire on the inner side near the jute rope. The point is that the copper has oxidized in some way near the jute.

Dr. Whitney: "I don't think any of you know how much poorly drawn brass is made or how little there is known about it. It is necessary to find the laws to make brass."

Dr. Little referred to the efforts of the American Brass Founders' Association and stated that he hoped to have a representative in all trade organizations to represent the Division and to inform it of what is being done by them and to tell them what we are doing.

Dr. Whitney suggested that it would be helpful if the members got together by letter consultation, and in this manner secure information which would be valuable to each other.

Mr. Little was asked if the Society was associated with the Paint Manufacturers' Association. He replied that it was not, but that he had taken the matter up with the president of the latter society.

A motion was made, seconded, and carried, that a committee of three be appointed by the chairman for the purpose of bringing before the Division a list of elements which now appear to be little used and of low commercial value, in order that it might be possible to devise some means by which they could be manufactured and used beneficially and profitably.

It was further suggested that this committee act as a clearing house to communicate with the manufacturers and find out what kind of offers they could get on these elements and put the matter before the Division.

Mr. Brady suggested that something should be done regarding the problem of helping students who have recently graduated from colleges, to secure employment, and stated that he had numerous applications from them and did not know how to arrive at the best manner to aid them. He

cited in brief his own experiences upon leaving college, and said he thought a good plan would be for the chemists if they could not give the applicants employment, to tender them the use of their offices as headquarters and aid them in every other way possible to obtain positions.

Upon adjourning, many were the expressions from those present upon the successful meeting, with a look forward to the mid-winter gathering in Boston.

B. T. BABBIT HYDE, *Sec'y.*

DIVISION OF FERTILIZER CHEMISTS.

The meeting of the Division of Fertilizer Chemists, in connection with the Detroit meeting of the American Chemical Society, was called to order by the chairman, Mr. F. B. Carpenter, Wednesday morning, June 30, 1909. Secretary J. E. Breckenridge then read the minutes of the previous meeting, which were approved. The secretary also reported

an enrolment of 105 members in the Division. The following committee reports were then received and adopted:

REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION.

Due to the meeting abroad and other causes, it has been impossible to have a full meeting of the committee.

Much individual thought has been put on the matter and plans for an early meeting of the committee are made in order to have something of value ready for the next meeting of the Division. ARTHUR LOWENSTEIN, *Chairman.*

REPORT OF THE COMMITTEE ON POTASH.

No cooperative work has been done to date on potash, but the members of the committee have been in touch by correspondence and plan to try out washing sample on filter with small portions of water into a flask and adding HCl to the washings, then proceeding as in the official, method.

We believe that this method will give more correct results as to water-soluble potash than the method of A. O. A. C. J. E. BRECKENRIDGE, *Chairman.*

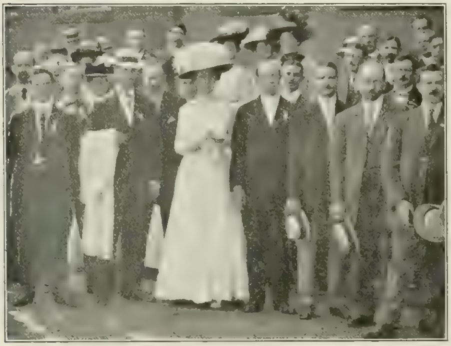
REPORT OF COMMITTEE ON PHOSPHORIC ACID.

The Committe has had trouble in finding out as to whether or not all the members appointed on this committee would serve, and so the work of the committee has been delayed. It is hoped that by the next meeting, something of interest may be developed. S. H. SHEIB, *Chairman.*

REPORT OF THE COMMITTEE ON NITROGEN.

It was to be expected that the formation of a new Division and the work which this division was undertaking would not move off as promptly and evenly as it undoubtedly will in the future. The appointments were received about the middle of March, but acceptances were late getting in and to date I have not heard from one appointee as to his intentions.

The most important subject before the committee is the question of methods for determining total nitrogen, including nitrates by the official Gunning and Kjeldahl methods. Mr. Jones, one of the members of this committee, happens to be the Referee of the Association of Official Agricultural Chemists, on the same subject, and the results he will obtain from the coöperating chemists will be certain



to be of interest. While some analysts seem to have no difficulty with the official methods, many others do have trouble, and the work on this subject should be undertaken by this committee at once.

Another subject of interest in the hands of this committee is that of the methods for determining the availability of nitrogen. There are three or more methods for this purpose and the results by the three methods are usually widely different for any given ammoniate and usually none of them agree with the results of vegetation tests or actual field tests. The problem of finding the methods best suited for the judgment of the value of ammoniates and one that is fair to both buyer and seller is one that this committee should consider.

There is another matter in connection with the official methods which should be mentioned, namely, the question of preparing standard acid and alkali. The official method for preparing these acids now is the determination of the chlorine in the hydrochloric acid by precipitation as silver chloride. It is, of course, understood that none but the purest hydrochloric acid should be used for this purpose. It would seem, however, that a method for standardizing acid and alkali should include not only the determination of the chlorine in the determination of hydrochloric acid, but its actual acidity as well. The determination of chlorine will not differentiate between hydrochloric acid, and its salts and other tests must be made in order to determine the strength of the acid in addition to the determination of the chlorine. It seems, therefore, that the method for preparing standard acid should be given in more detail than it is at present, the most important feature being to find the acidity of the standard acid by as direct means as possible.

P. Rudnick, *Chairman*.

Report of the Committee on Ammonium Citrate Solution.

Your Committee on the Ammonium Citrate Solution for the determination of insoluble phosphoric acid in fertilizers, appointed at the Baltimore meeting, begs leave to report as follows:

The purpose of the committee was to draw up such specifications for the ammonium citrate solution that chemists working at different points might be able to prepare more uniform and comparable solutions than in the past. The method in general use for preparing the ammonium citrate solution in this country is the method of the Association of Official Agricultural Chemists, as detailed on pages 3 and 4 of Bulletin **107**, U. S. Department of Agriculture. In this method, two means are given for making the solution neutral. According to the first way, the solution is to be made neutral by means of corallin indicator and according to the second, after the solution is made approximately neutral by means of corallin, it is to be finally adjusted by cochineal indicator, after the citric acid is precipitated by means of alcoholic calcium chloride. Your chairman, as well as others, has examined a number of solutions made up according to these instructions and has found that few solutions indeed, if any, are identical in composition. It is safe to say that the majority of solutions used throughout the country for the determination of insoluble phosphoric acid are only approximately similar in composition. Further, it is the opinion of your committee as well as others, that the method of preparation by means of indicators has been tried thoroughly and found wanting, and that, therefore, it becomes necessary to devise new means by which more uniform solutions can be prepared.

The effect of dissimilar solutions on the determination may result in differences of about 1 per cent. in the case of acid phosphate, but in the case of mixed fertilizer, containing steam bone for instance, differences as high as 6 per cent. in the insoluble have been obtained by chemists of high

standing. The differences are also great in the case of some other phosphatic materials.

Mr. J. M. McCandless, Referee on Phosphoric Acid for the Association of Official Agricultural Chemists, for the year 1908, said in his report to the Association, among other things, the following in regard to the citrate solution:

"As the Referee was to say whether the solutions were neutral or not, and as scarcely any two chemists can agree on the exact point of neutrality, whether from lack of sensi-

tiveness of the indicators or color-blindness on the part of the operators, he decided to make an analysis of each sample according to the method outlined in his last report to the Association, and be guided by those results in deciding upon neutrality.

"The following method of analysis was adopted: 25 cc. of each solution were pipetted into a 250 cc. flask made to mark, shaken and 25 cc. of this solution were pipetted into a distillation flask; to the solution in the flask, 40 cc. of N/4 caustic soda solution were added, and the contents of the flask distilled into 20 cc. of N/2 acid, continuing the distillation until the volume of the distillate measured from 67–70 cc. The ammonia in the distillate was then titrated by means of N/10 alkali. The residue in the retort was washed into an Erlenmeyer flask, excess of standard acid added, then a few drops of phenolphthalein, and the excess estimated by N/10 alkali. From the result, the weight of citric acid originally combined with the ammonia was calculated. * * *

"It appears that some chemists prepare their ammonium citrate solution by treating the citric acid with excess of ammonia and then leave the hot solution to neutralize itself, or finally adjust it, some by means of red and blue litmus paper, others by corallin. Some state that they have never been successful in the use of corallin; others adjust finally by means of the alcoholic solution of $CaCl_2$. * * * There are materials (notably fertilizers containing bone) on which a slight difference in neutrality of the ammonium citrate solution makes a great difference in the results. It is a reproach to the Association that it has suffered the matter to remain in its present condition so long. While the referee has a strong personal conviction that the only proper method of making the solution neutral is by analysis and calculation of the exact quantity of ammonia or citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist."

After some correspondence among the members of your committee, it was decided that the work of the committee should be along the lines of analysis of the ammonium citrate solution and that the preparation of solutions by means of indicators must be abandoned, if concordant results are to be obtained by different chemists. It was pointed out in the correspondence that the ammonium citrate solution as made up according to the instructions of the Association of Official Agricultural Chemists does not contain the proper ratio of ammonia to citric acid for tri-ammonium citrate nor for di-ammonium citrate, but for a mixture of these two, a little more of the former than the latter; that is, there is not present in the solution sufficient ammonia to correspond to the tri-ammonium citrate formula, but less than this quantity. However, it seemed desirable to perpetuate the present practice in so far as possible, in order that results obtained in the past might be compared with results to be obtained in the future, and as a plan of work it was decided that each of the three members of the committee should prepare a solution of ammonium citrate according to the Association of Official Agricultural Chemists' method, and in that solution determine the exact amount of ammonia and citric acid, according to the following method of analysis:

Method of Analysis of Ammonium Citrate Solutions.

Fifty cc. of the ammonium citrate solution (at 20° C.) are diluted to 500 cc. with boiled, distilled water, neutral to phenolphthalein and brought to a temperature of 20 C. 50 cc. of this solution are transferred to a distilling flask and diluted with 200 cc. of distilled water (neutral to phenolphthalein), and are then made alkaline by adding exactly 35 cc. of $N/2$ NaOH. The flask is then connected to a distilling apparatus and the NH_3 distilled off and collected in $N/2$ H_2SO_4. The excess of H_2SO_4 is titrated with $N/2$ NaOH and cochineal and the NH_3 calculated. The residue from the distillation is a solution of sodium citrate and sodium

hydrate in water. The free NaOH may be titrated, using $N/2$ H_2SO_4 and phenolphthalein The number of cc of $N/2$ H_2SO_4 required subtracted from 35 gives the number of cc. of $N/2$ NaOH required to neutralize the citric acid. The ammonia and citric acid are reported as grams per liter of solution at 20 C.

This was done and the results obtained by the three members were as follows:

	Citric acid	Ammonia
Mr Jones	184.7	43.58
Mr Gascoyne	185.5	45.03
Mr Richardson	189.0	43.60
Average	186.4	43.7
In round numbers......	186	43.7

Expressed in grams of crystallized citric acid and grams of actual ammonia per liter at 20 C. As you will note, the average of these figures is 186.4 g. citric acid and 43.7 g. ammonia per liter of solution, or in round figures 186 g. citric acid and 43.7 g. ammonia per liter of solution. After some further correspondence, it was decided by the committee that these figures be recommended to this body for adoption as the standard for the ammonium citrate solution.

One member of your committee has done the following work in connection with this problem: A check sample of mixed fertilizer containing bone and acid phosphate was sent out to eight chemists who were working on fertilizer analysis. The results returned showed good agreement in everything except available phosphoric acid and the maximum difference in this determination was 6 per cent. A similar sample was sent to the same chemists, together with a bottle of ammonium citrate solution, each bottle

being taken from the same stock bottle and made up by one chemist. The results returned showed good agreement in every case, the maximum difference in the case of available phosphoric acid being 0.60 per cent. It has been suggested that differences in manipulation, in filtration and in other ways affected to a large extent the determination of insoluble phosphoric acid, but it would appear from these results that if ammonium citrate solutions used by different chemists are alike, good agreeing results can be obtained. That such a result is highly desirable is indicated by the great number of discrepancies which occur every month and every year in the case of available phosphoric acid when different chemists are working on the same lot or sample of fertilizer.

In view of the foregoing, your committee desires to recommend the following:

Recommendation 1.—That provisional specifications for ammonium citrate solution be established as follows: Standard ammonium citrate solution shall contain 186 g. crystallized citric acid and 43.7 g. ammonia per liter, measured at 20° C. and determined by the following provisional method of analysis:

Fifty cc. of the ammonium citrate solution (at 20° C.) are diluted to 500 cc. with boiled distilled water, neutral to phenolphthalein and brought to a temperature of 200° C. 50 cc. of this solution are transferred to a distilling flask and diluted with 200 cc. of distilled water (neutral to phenolphthalein), and are then made alkaline by adding exactly 35 cc. of $N/2$ NaOH. The flask is then connected to a distilling apparatus and the NH_3 distilled off and collected in $N/2$ H_2SO_4. The excess of H_2SO_4 is titrated with $N/2$ NaOH and cochineal and the NH_3 calculated. The residue from the distillation is a solution of sodium citrate and sodium hydrate in water. The free NaOH may be titrated, using $N/2$ H_2SO_4 and phenolphthalein. The number of cc. of $N/2$ H_2SO_4 required subtracted from 35 gives the number of cc. of $N/2$ NaOH required to neutralize the citric acid. The ammonia and citric acid are reported as grams per liter of solution at 20° C.

Recommendation 2.—That this committee be continued and be instructed to do further work with solutions prepared in this way and also to endeavor to have the Association of Official Agricultural Chemists, at its next meeting, appoint a committee of three to work with this committee as a joint committee, with a view of having the above specifications adopted by the Association of Official Agricultural Chemists.

In conclusion, your committee desires to say that the quantities in these specifications as laid down, may be modified by subsequent work to some extent, but at the same time if the principle of making up the ammonium citrate solution according to analysis is once established, it will be a simple matter at a future time to modify the exact quantities of citric acid and ammonia without disturbing in any way the general trend of fertilizer analysis.

All of which is respectfully submitted,

W. D. RICHARDSON, *Chairman*

After the adoption of the committee reports given above the Committee on By-laws submitted a set of by-laws for the Division and it was decided to send a copy to each member of the Division for any remarks or comments, action to be taken at the next meeting.

The following papers were then read and discussed:

1. J. E. Breckenridge: "Potash Tests in Commercial Fertilizers."
2. J. E. Breckenridge: "Experiments to Find, if Possible, the Potash in Fertilizers Having Their Potash from Carbonate of Potash."
3. F. B. Porter: "The Measurement of Crude Sulphuric Acid."
4. R. H. Fash: "The Corrosive Action of Alkaline Tank Water upon an Evaporator and a Remedy."
5. R. H. Fash: "The Use of Wood Ashes in Commercial Fertilizers."
6. J. M. McCandless: "Preparation and Neutralization of the Ammonium Citrate Solution."
7. G. S. Fraps: "The Needs of Texas Soils for Fertilizers."
8. G. A. Farnham: "The Effect on Insoluble Phosphoric Acid when Litmus, Corallin and Cochineal Are Used in Preparing the Solution of Ammonium Citrate."
9. Burt L. Hartwell: "The Availability of Certain Nitrogenous Manures."
10. Carlton C. Jones: "Moisture in Phosphate Rock of the Pacific."

The meeting adjourned to meet next winter in Boston, in connection with the meeting of the American Chemical Society.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, LONDON, MAY 27th to JUNE 2nd, 1909.

SESSION OF MAY 28, 1909.

Section V. Industry and Chemistry of Sugar.

Opened by Sir Richard C. Carton, President of the Section.

Vice-presidents for the day, Dr. Herzfeld and Messrs. H. Pelle and F. Sachs. Secretary for Section, Dr. Thorne.

G. C. BORGUINO, *Ravenna. "Origini del' Industria dello succhero in Italia."*—The Italian sugar industry dates back to the thirteenth century, when sugar cane was cultivated in Sicily. The beet sugar industry began in 1850, became firmly established in 1880, and in 1890 had so increased that Italy changed from a sugar-importing to a sugar-exporting country.

H. P. AGEE, *New Orleans. "The Cane Sugar Industry of Louisiana."*—The cane is raised under somewhat adverse climatic conditions on alluvial soil, giving 22.5 tons of cane per acre and yielding 160 lbs. sugar per ton of cane. Thus 350,000 long tons of sugar are produced consisting of raw sugar for refining and white and prime yellow sugar made without bone-black, and high-grade syrups and molasses for table use.

A. H. BRYAN, *Washington. "The Beet Sugar Industry of the United States."*—Refined or white sugar is made directly from the beets and not raw sugar.

The Steffens lime process is replacing the osmose process. The pulp is used for cattle feed, the molasses for cattle feed and alcohol. The production of beet seed is increasing. The manufacture is confined principally to the arid regions of the West, California and Michigan, and last year produced 414,000 tons, consumed locally.

W. D. HORNE, *New York. "History of Sugar Refining in the United States."*—Sugar was refined in New York City as early as 1689 and by 1810 there were annually refined 5,000,000 lbs. of sugar, which sold at 20 cents per lb. In

1860 there were 41 refineries producing $42,000,000 worth of refined sugar per year. The next decade was marked by great technical improvements, leading to overproduction and financial failure. In 1887 seventeen of the principal refineries consolidated to form the Sugar Refineries Company, which largely remedied the evil of overproduction. The Company reorganized in 1891, forming the American Sugar Refining Company, which has largely controlled the business since, purchasing many competing plants and entering the beet sugar industry.

The price of raw sugar as well as the margin between raw and refined has steadily declined. The United States consumes about 3,000,000 tons of sugar annually of which 414,000 are domestic beet, 347,000 domestic cane and the balance foreign cane, refined in the United States.

THEODORE BROOKS, *Guantanamo, Cuba.* "*Review of the Conditions, Progress and Future of the Sugar Industry in Cuba.*"—By 1880 there were 470 factories working to produce 625,000 tons of sugar. In 1895 the production was 934,180 tons from fewer factories, due to the centralization of factory work. Even then only 8 per cent. of sugar was produced from the cane. The production this year is estimated at 1,350,000 tons from 170 factories, 10.16 per cent. sugar being obtained from the cane ground. Great improvement of processes of manufacture has taken place, especially in milling. Chemical control is becoming prevalent. The agricultural methods are susceptible of much improvement. Labor is a difficult problem in Cuba. The average cost of manufacture might be given as 2.25 cents per pound though some factories operate at a much lower figure. Discussed by Messrs. H. Pellet, Stein and Brooks.

NOËL DEERR, *Honolulu.* "*The Cane Sugar Industry in the Hawaiian Islands.*"—In the author's absence, read by Dr. Horne. The output increased from 54,000 tons in 1882 to 521,123 tons in 1908, due to a reciprocity treaty with the United States and to the irrigation of arid regions.

The Lahaina variety of cane is mainly cultivated under irrigation and the Yellow Caledonia under natural rainfall, the former yielding about 12,000 pounds sugar per acre, the latter 5,000 to 8,000. The average annual production is 11,000 tons sugar of 95° to 98° per factory. The mills are usually 11 rollers. The chief markets are New York and San Francisco. Discussed by Messrs. H. Pellet and Kobus.

F. ZERBAN, *Lima.* "*The Cane Sugar Industry in Peru.*"—About 50 estates, comprising some 8,000 acres in coastal valleys, produce 150,000 tons of sugar of which 120,000 tons are exported to England and Chili. The factories are mostly old and not well equipped. The average yield is 35 to 45 tons per acre, and from four to five cuts are made. Discussed by Messrs. Saillard and Fischmann.

On the motion of Prof. Herzfeld, a committee was appointed, consisting of Messrs. Dupont, H. Pellet, Fischmann, Sachs, Borguino and Saillard to take steps toward furthering the movement for obtaining a reduction of the taxes on sugar advocated by M. M. Dupont and Fischmann.

FRANÇOIS DUPONT, *Paris.* "*Moyens de developper la consommation du sucre.*"—Advocating the wider use of sugar in bread. Discussed by Messrs, Saillard, Fischmann, Herzfeld, Sachs and Dupont. After the reading of the paper the chairman appointed a committee to consider means of increasing the consumption of sugar, consisting of Messrs. Dupont, Sachs, Fischmann, Thorne and Horne.

K. ANDRLIK and T. URBAN. "*Ueber die Variabilität des Stickstoffsgehaltes in dem Zuckerrubenwurzeln.*"—Variabilities in nitrogen and sugar content are independent of each other, and nitrogen varies more than sugar. The relations of the sugar and nitrogen content depends upon the relation of these substances in the stems.

SESSION OF MAY 29, 1909.

President for the day, Sir Richard C. Garton (in the chair), Messrs. Anlard and Fischmann.

SIR DANIEL MORRIS. "*Recent Researches in the Production of Seedling Sugar Canes in the West Indies.*"—Copiously illustrated by colored sketches and diagrams. Discussed by Sir R. C. Garton, Messrs. Pellet, Saillard, Manoury and Kobus.

The President welcomed the President of the Congress, Sir William Ramsay, who was present in the sitting of the section.

FRANÇOIS STROHMER, *Vienna.* "*Gibt es in der Zuckerrube optisch aktiven Nictzucker welche die Polarizationsresultate beeinflussen?*"

H. PELLET. "*De l' influence des substances pectiques sur le dosage du sucre dans le betterave par les methods du Dr. Zcheye et de M. M. F. Strohmer and O. Fallada.*"—Discussed by Prof. Herzfeld.

F. SACHS, *Brussels.* "*Analyses des Cossettes fraihhes de betterave.*"—Advocating digesting 26 grams of beet pulp for 30 minutes with 177 cc. water containing subacetate of lead, in a covered metallic container in a water bath at 80° C., cooling, filtering and polarizing in a 400 mm. tube. (C) "*Dosage du cristallisable daus la betterave.*" A plea for the cold aqueous extraction of beet pulp. On the motion of Prof. Herzfeld a committee, consisting of Messrs. Pellet, Sachs, Strohmer, Herles, Saillard and Herzfeld, was appointed for drawing up the text of a proposition to be put before the International Commission for Unification of Sugar Analyses for making the aqueous method of Pellet for the analysis of beet the standard one.

HUGH MAIN, *London.* "*Estimation of Ash in Sugar House Syrups by Determination of Electrical Conductivity.*"—By means of a 2-cell accumulator, an induction coil giving a clear high note, a bridge having a resistance of 200 ohms in each of two of the proportional arms, a resistance cell with platinum electrodes for the sugar solution in the third arm, a resistance box with resistance of from 1 to 4,000 ohms in the fourth arm and a telephone one can make an ash determination in 10 minutes. Conductivity is proportional to ash content in solutions of the same class. Discussed by Messrs. Steffens and Herzfeld.

J. D. KOBUS, *Java.* "*Cane Seedlings in Java.*"—Illustrated by lantern slides. By cross fertilization of the Cheribon cane with others new varieties have been established, immune against diseases which the Cheribon was subject to. Thus several factories have been saved from ruin and others enabled to pay high dividends. The new canes grow in soils which could not be used before, increasing the sugar production—which has risen from 350,000 tons in 1885 to over 1,200,000 tons in 1908. Discussed by Messrs. Pellet, Fischmann and Manoury.

H. PELLET, *Paris.* *"Sur les pertes en Soorerie de Betteraves; et sur les pertes en Sucrerie des Cannes."* The author advocates the use of Clerget's method of polarization for juices and finished products, to avoid fallacious impressions of loss.

F. HERLES, *Prague.* *"Ueber die optisch aktiven der Einwirkung des Kalkes in der Warme unterliegenden Nichtzuckerstoffen und über die Biestimmung ihrer Polarization."*—Discussed by Messrs. Vivien, Saillard and Pellet.

F. EHRLICH, *Berlin.* *"Ueber die Dartellung und Konstitution des Karamels und seine Bestimmung in Zucker-Säften und Sirupen."* Discussed by Prof. Herzfeld.

AUGUSTE AULARD, *Brussels.* (a) *"Sur le phenomene osmotique qui s'accomplit durant l'extraction du jus de betterave par diffusion ou ebouillement."* (b) *"Du traitement jus de betterave par l'acide sulfureux gazeux."* (c) *"Emploi de l'acide sulphureux liquide dans l'industrie sucrerie."* (d) *Filtration sur le sable du jus de diffusion et des divers produits de la sucrerie de betterave."*—Discussed by Messrs. Manoury, Naudet and Pellet.

H. DECLUY, *Paris.* *"Contribution a' le theorie des fours a' chaux, tables pratiques donnant la richesse en acides carboniques des gaz, emploi daus les fours a' chaux des cokes d'usines a'gaz."*—The paper discussed the relation between the solid and gaseous elements in the lime kiln, between the gases themselves, the calorific theory and equations of the kiln, the losses by radiation and convection and the varieties of coke employed, besides giving a table of richness of gas produced under varying purities of limestone and percentages of cake employed

FRANCOIS DUPONT, *Paris.* *"Aire de culture de la betterave a sucre."* Session adjourned.

THE INTERNATIONAL COMMISSION FOR THE UNIFICATION OF METHODS OF SUGAR ANALYSIS

held its triennial meeting at 10 A.M. on May 31, 1909, in the Imperial Institute, London, in connection with the VII International Congress of Applied Chemistry in the room of Section V.

Prof. Herzfeld, president of the Commission, presided, receiving the following reports:

1. The report of the work of the Commission since the last meeting in 1906 was given by Prof. Herzfeld and Prof. Strohmer.

2. Messrs. E. Saillard and Buchka reported upon their investigations of tables of relation between the density of pure sugar solutions and their content in sugar.

Resulting from the discussion of this report it was resolved on the motion of Mr. François Sachs "That a standard table at a temperature of 20° C. be officially adopted by the Commission and that this table be based upon the official German table: and further that other tables at different temperatures (such as 15 and 17 1/2) be calculated from the standard one according to the Mohr System at 20°/20°."

3. The clarification of the "Solutions of Cane Sugar for Analysis" was reported upon by Messrs. Prinsen Geerligs and F. Sachs, the former of whom read a paper on the subject. After discussion of the report "it was considered that while the lead *acetate* method might be useful in the clarification of syrups (for the determination of reducing sugars) and was permissible, if excess were absolutely avoided, it was not advisable at present, to make the general adoption of this method official."

They also recommended "That although we are aware that lead *subacetate*, both in the dry state and in solution, precipitates a part of the optically active constituents from solutions of raw cane sugars and molasses, yet we advise the continued use of this reagent for the clarification of such solutions for the purpose of their polarimetric determination, but we especially emphasize that an excess of this defecant must not be used, and that only the minimum amount necessary for obtaining a distinct reading be added."

This, according to Prof. Herzfeld, leaves it optional for any association of chemists or others connected with the International Commission to adopt the dry lead method, as introduced by Dr. W. D. Horne.

Some papers were then read in connection with the Commission, namely:

C. A. BROWNE, *New York.* *"The Use of Temperature Corrections in the Polarizations of Raw Cane Sugars and Other Products upon Quartz Wedge Saccharimeters."*—In the absence of Dr. Browne a résumé was given by Dr. W. D. Horne, showing that in products containing invert sugar there are two conflicting tendencies with an elevation of temperature above the normal temperature of polarization. In very high-grade products the polarization decreases with rise of temperature due to the decreasing of the specific rotatory power of sucrose, but an elevation of temperature carries with it also a decrease in the left-handed or minus ratotion of levulose, tending to offset the decrease in "polarization" due to the diminished rotation of sucrose.

As levulose diminishes in its gyrodynat about 27.3 times as much as sucrose diminishes in its gyrodynat for an equal elevation in temperature, it follows that in raw sugar cane sugar having a "polarization" of about 84 "the invert sugar usually present is just about enough to neutralize the diminution of rotation of the sucrose present: and these sugars are found to show no change in polarization for changing temperatures. For lower sugars than those of 80 "polarization," it is found that the polariscope reading actually increases as the temperature of observation rises. From these results and the recognized futility of applying different temperature correction formulae to different classes of sugars, the author asked the Commission to rule that "Formulae and tables that have been established for correcting the polarization of pure sucrose for changes in temperature are applicable to the polarization of refined sugars only" and not for raw products.

Dr. H. W. Wiley read a paper by Mr. A. Hugh Bryan, chief of the sugar laboratory in the Dept. of Agriculture, Washington, in which he also pointed out the inapplicability of the present temperature correction tables for any but the highest grades of cane sugars or sugars containing no invert sugar. A general discussion followed, and while it was agreed that the temperature corrections now employed in the United States were not correct for low-grade sugars no definite resolution on the subject was considered advisable at present. Dr. Wiley stated that arrangements were being made in the official laboratories in the United States to make all polarimetric readings of both raw and refined sugar at 20° C.

Dr. Wiley also read a paper by C. A. BROWNE and A.

HUGH BRYAN on "*The Use of Lead Subacetate in the Clarification of Sugar Solutions,*" showing that repeated experiments had shown that defecating raw cane sugar solutions with Horne's anhydrous subacetate of lead gives much more accurate results than the old method of defecating with the solution of lead subacetate. It also showed the desirability of using the neutral acetate of lead in defecating sugar solutions in which reducing sugars are to be determined.

Session closed.

In the afternoon, Section V resumed its session.

MR. LEWIS EYNON read a paper upon the "*Influence of Clarification with Basic Lead Acetate Solution on the Valuation of Sugar Product and the Relation between the Amount of Lead Added and That Precipitated.*"

The author showed that by adding about 7 times the necessary quantity of subacetate to a Jaggary sugar, the direct polarization was raised from 73.2 to 75.1, due to removal of levulose and concentration of solution because of volume of precipitate: the Clerget polarization was raised 0.5 principally owing to the volume of precipitate and the reducing sugars were reduced from 9.7 per cent. to 8.5 per cent. by precipitation. He urged avoidance of excessive amounts of reagents.

L. PELLET, *Lille.* "*L'emploi d'injecteurs pour l'imbibition rationnelle de la bagasse.*" The author described an injector for wetting bagasse, consisting of a main pipe with numerous nozzles delivering conical sprays to give uniformity to the distribution of the water.

P. KESTNER, *Lille.* (*a*) "*Les Procedes Kestner-Lagrange pour l'epuisement des basproduits.*" A description of this new method of carrying the evaporation to the farthest point by means of the author's "descending film" evaporator, in which the liquor climbs to the top of tubes in the centre of the tube nest and there descends by the outer tubes. It is the only apparatus in which it is possible to concentrate continuously under pressure without any alteration or coloration of the syrups and mother liquors. (*b*) "*Les progres a realizer dans l'evaporation en sucrerie de cannes.*"—Further discussion of the author's climbing film evaporator.

L. EYNON and J. H. LANE, *London.* "*Note on the Influence of Time and Use on the Capacity of Graduated Vessels.*" Sugar flasks of 100 cc. capacity lost only 8 to 12 milligrams in weight during four years and their contents did not alter materially. The flasks had been kept a long time before graduation to allow any shrinkage to have fully taken place.

R. G. CADWELL and R. WHYMPER, *London.* "*Determination of Rotatory Power.*"—Read by title.

H. PELLET, *Paris.* "*Dosage de la matiere sedu dans les produits de la sucrerie de betteraves, de la sucrerie de cannes et de raffinerie.*"—Describing a special metallic evaporating dish in which the sugar product, diluted and incorporated with pumice stone, is dried at 105° or 106° C. to a constant weight in a bath. Discussed by Messrs. Saillard, Pellet and Prinsen Geerligs.

E. SAILLARD, *Paris.* "*Apropos de l'analyse des molasses on massecuites de betterave.*"—Showing the variations existing in the ratio of organic matter to ash, as well as in the relation of true moisture to apparent moisture as determined by density. Discussed by Messrs. Saillard, Pellet and Prinsen Geerligs.

VLADIMIR STANEK, *Prague.* "*Aus das Austrocknen der Rohzuckerproben und ein Verfahren zur Vermenhung derselben.*"—Discussed by Mr. H. Pellet.

J. B. PUVREY, *Groulart.* "*La procede rapide de traitement des bas produits de sucrerie de betterave, de sucrerie de cannes et de raffinnerie par le systeme Karlik Czapikowski.*"—Discussed by Messrs. H. Pellet, Saillard and Borgnino.

W. D. HORNE, *New York.* "*Dry Lead Defecation in Raw Sugar Analysis.*"—A résumé of the work and literature upon this subject and a plea for its adoption by the International Commission as the official method. Discussed by Messrs. H. Pellet, A. Watt, Prinsen Geerligs and Davoll.

SESSION OF TUESDAY, JUNE 1, 1900.

Presidents for the day, Messrs. Baumann, Dupont, Garton and Manoury, Hermann Claassen and Dormagen.

"*Ueber die Bedeutung des Uebersättigungs-Coefficienten fur Verkochung und Krystallisation.*"

L. RIVIERE, *Paris.* 1. "*Traitement des jus de diffusion et autres liquides sucres par l'acide fluosilicique et les fluosilicates solubles.*"

2. "*Fabrication et emplois industriels des melasses depotossées.*"

3. "*Transformation des fluosilicates alcalins en carbonates.*"

F. ZERBAN, *Lima.* "*Studies on Sulphitation in the Cane Sugar House.*—Not read.

E. SAILLARD, *Paris.* "*Composition minerale de la betterave.*"—Sugar beets contain more nitrogen, per cent. sugar, in dry than in wet years. Rich beets contain in their ash less soda, more phosphoric acid and more lime than poorer beets. The author found in beet roots (of 15.7 per cent. sugar in the entire plant) per 100 of sugar, 2.4 to 2.8 nitrogen, 0.6 to 0.07 phosphoric acid, 3.2 to 3.6 potash, and 8.0 K_2O, Na_2O, MgO, CaO, P_2O_5. The different principles of the beet root do not diffuse with equal speed and the purity of diffusion juice and purified products is influenced by the degree of exhaustion of the cossettes.

H. PELLET, *Paris.* (*a*) "*Sur la pureté reelle des petits jus de diffusion.*" (*b*) "*Sur la pureté reelle et la pureté apparante dans le le control de la sucrerie de cannes et de betterave.*"—A discussion of the influence of mineral salts upon the determination of the total solids in sugar solutions and the effects of Raffinon and glucose upon the polarizations. (*c*) "*Influence de la concentration des produits purs et impurs sur la determination de la densite.*"—Showing that the discrepancy is less in the more concentrated solutions and that all solutions should be made up to about 20 per cent. total solids before taking density with Brix spindle.

D. L. DAVOLL, JR., *Guantanamo, Cuba.* "*The Analysis of Bagasse.*"—Alcoholic extraction of finely cut bagasse is found to be more thorough than aqueous extraction, and the fiber determination gives a lower figure, although ash and protein both are higher in the fiber. Formaldehyde was found unreliable for preserving bagasse.

GUISEPPE MASSOBRIO, *Genoa.* "*Utilizazione dei residui della de purazione die sughi (schiume dei defecazione) per la fabricazione del cimento.*"—The filter press cakes are mixed wet with sufficient clay or other suitable material to give the composition of Portland cement to the mixture and this is settled by decantation in ground basins and later removed, roasted to clinker and converted into cement. A value of about fifty cents per hundredweight is placed upon the product.

EMIL BAUR, *Raab.* "*Verlustquellen bei der Erzeugung von Schlempekohle.*"

AFTERNOON SESSION.

J. EFFRONT, *Brussels.* "*Utilization d'azote de betterave.*"

C. A. BROWNE and A. HUGH BRYAN, *Washington.* "*The Analysis of Commercial Dextrins.*"—Read by title.

L. K. BOSELEY, *London.* "*Sugar and Corn Syrup* (*Starch Glucose*) *as Raw Materials for the Confectionery and Preserves Industries.*"—Sugars of equally high polarization and apparently alike differ greatly in the darkening caused by raising their solutions to 325° F. through continued boiling. The author attributes this to traces of nitrates, organic matter or sulphates. The power of crystallizing out of a strong solution also varies considerably, being diminished by grinding the sugar before dissolving.

A. R. LING. "*Analysis of Molasses for Distillery Purposes.*"

K. ANDRLIK, V. BARTOS, AND J. URBAN. "*Ueber variabilitat des Gewichtes und des Zuckergehaltes der Zuckerrubenwurzel und uber die gegenseitigen Beziehungen dieser beiden Merkmale.*"

H. PELLET. "*Proposition relative a l'adoption d'une methode internationale d'analyse des mélasses de betteraves at des mélasses de cannes. Clarification; dosage de l'eau; dosage des cendres; polarization avant et apres inversion; dosage des reducteurs.*"

FRANCESCO V. VIDAL, *Mexico.* "*Utilization des vinasses epuisées en distillerie de mélasse de canne ou de jus de canne, en vue d'obtenir de l'azote sous forme d'engrais.*"

J. URBAN. "*Ueber die Bestimmung des Invertzuckers in der Rube.*"

K. ANDRLIK. "*Ueber die Darstellung des Adonins aus Melaisse-abfallangen.*"

K. ANDRLIK UND J. URBAN. "*Einfluss der Ernährung auf die Variabilitat der chemischen Zusammensetzung der Rube im Erston Vegetationsjahre.*"

K. ANDRLIK. "*Ueber Guaninpentosid aus den Melasseabfallangen.*" W. D. HORNE.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

First Semi-annual Meeting, Brooklyn, N. Y., June 24–26, 1909.

Abstracts of Papers.[1]

THE UTILIZATION OF LOW-GRADE FUELS.

By DR. O. K. ZWINGENBERGER, N. Y. City.

This paper gives the results of the experiments of the United States fuel testing plants on the utilization of lignite and peat as fuel, also the results of experiments carried out in Europe on the use of these fuels. The author describes the by-products produced by distillation, and their economic relation to the utilization of these low-grade fuels. He showed that up to the present time the low cost of coal and oil in the United States did not permit the utilization of low-grade fuels. He showed that for some states, however, such as Texas, Dakota, Minnesota, etc., the utilization of such fuels is very important, and that by the use of special gas producers and the utilization of by-products such fuels are far more economical than anthracite or the best coke. By the combination of gas producer and a coking chamber an increase of 20 per cent. in heating value and a much larger output of gas can be obtained with these low-grade fuels. The paper is a very important contribution to the literature of the utilization of lignite or peat.

[1] The papers of which the abstracts are published were presented in complete form at the meeting for publication in the Transactions of the Institute.

EFFICIENCY LIMITS IN THE POWER GAS PRODUCER.

By WILLIAM D. ENNIS, Professor of Mechanical Engineering in the Polytechnic Institute of Brooklyn.

The difficulty of separately and accurately determining the efficiency of a gas producer suggests a computation of its efficiency limits. When pure carbon is converted into carbon monoxide, 30.69 per cent. of its potential heating value is transformed into temperature and becomes unavailable for use in the gas engine. By using a certain proportion of steam mixed with the air supplied for gasification the temperature heat may be partially employed in decomposing the steam. The hydrogen then carries this temperature heat to the engine as available heat of combustion. With sufficient steam supplied the temperature elevation might be eliminated, and the efficiency would be 100 per cent. Steam will not decompose readily at temperatures below 1740° F., however, and the proportion of steam must be limited to that at which this temperature is attained. The efficiency is then, theoretically, 83 per cent.

A corresponding result follows the introduction to the producer ash pit of a portion of the waste gases discharged in the engine exhaust. The carbon dioxide then decomposes, and the heat absorbed is carried back to the engine. At the limiting temperature mentioned, the efficiency is 78 1/2 per cent. Modifying these results to include practical losses by radiation, fuel in ash, etc., variable specific heats of the gases, the presence of hydrocarbons in the fuel, the rise of surplus oxygen in the engine and in the producer, the initial temperature of the steam or waste gas and the formation of carbon dioxide, the maximum possible efficiency, with steam, appears to be less than 80 per cent., and with waste gas slightly less still. Actual analyses of gases produced by the two methods check the computations to some extent. The conclusion is drawn that the temperature of the gas is the best crude indication of efficiency of operation.

CREOSOTE OIL FROM WATER GAS TAR.

By SAMUEL P. SADTLER, Philadelphia, Pa.

This paper gives a summary of the specifications for creosote oil used in the United States and Europe and shows that the present weight of opinion is in favor of the use of heavy oils rather than the phenols and naphthalene which have been specified in the past. A résumé of the literature of the subject is given and it is shown that a study of the creosotes recovered from timber which has been in service for periods ranging from nine to forty-seven years show the presence of a very large percentage of oils boiling above 205° C. The paper gives the results of the examination of a creosote fraction obtained from water gas tar. It is shown that this fraction is very similar to that obtained from the creosote fraction of coal tar. While the author is not willing to express a final opinion on these results, but holds them subject to confirmation by addi-

tional distillations, he does state that this grade of water gas tar creosote may be quite specifically adopted to wood preservation.

An Automatic Acid Egg.

By Richard K. Meade, Nazareth, Pa.

This paper describes an acid egg in which the valve is opened and closed automatically by means of an electrical device.

Method of Clay Control as Practiced by the Western Canada Cement and Coal Co., Ltd.

By J. G. Dean, Exshaw, Alberta, Canada.

This paper gives the method adopted to overcome the difficulties presented by the use of clay low in silica and high in iron oxide and alumina, rendering it necessary to add limestone to secure the proper silica-alumina ratio. As this proved unsatisfactory, a shale having a high silica alumina ratio and a slate having a low ratio were mixed in the proper proportions to secure the ratio necessary for cement. The arrangement of the bins and conveyors is described and the formula used for calculating the proportions to secure the ratio necessary for cement. The arrangement of the bins and conveyors is described and the formula used for calculating the proportions by which the materials are mixed; also formula for calculating the percentage of limestone to be added. On proper grinding a perfectly uniform quality of cement was produced which was in perfect chemical balance, having no erratic or freakish features.

The Centering of Great Industries in the New York Metropolitan District.

By Charles F. McKenna

The author considers the large cities of eastern New Jersey and the territory about them, particularly the Passaic and Hackensack Meadows, to be part of a larger metropolis with New York and Yonkers, and perceives a tendency to the concentration therein of many great industries treating raw materials for staples. He instances, among others, the increasing production of large percentages of the country's yield of sugar, starch, animal, vegetable and mineral oils, silk, woolen and textile fabrics, metals and chemicals. He reviews the influences in the past of the ocean port and of water and rail transportation, the value of pipe lines, etc.

He considers that the present scheme of water supply can be improved upon, and advocates a combined system established by State agreement, among the features of which would be the tapping of the Catskill supply at Cornwall to supply Staten Island and some of the New Jersey cities between.

He believes that electric power should be introduced from the water-ways of both States, particularly to the meadows district, for which he advocates rapid improvement and foresees great development, particularly in the establishment of electro-chemical and electro-metallurgical plants. The electric energy deliverable here from the Passaic, the Delaware and the upper Hudson Rivers is estimated to be greater than the entire aggregate power at present used at Niagara Falls, New York, Lowell, Lawrence and Holyoke, Massachusetts. The following statistical figures are used:

Total Imports Fiscal Year, 1907

New York City	$853,696,952
Boston	124,432,977
Philadelphia	79,869,942
Baltimore	37,774,305
San Francisco	54,094,570
New Orleans	46,046,772
All other points	238,505,907
	$1,434,421,425

Total Exports, Fiscal Year, 1907.

New York City	$616,270,674
Galveston	236,277,727
New Orleans	169,897,311
Boston	99,820,742
Philadelphia	94,542,966
All other ports	636,908,614
	$1,853,718,034

Industries of Metropolitan District.

Comparative returns for 1900 and 1905 from municipalities with population exceeding 8,000.

	Number of establishments.		Aggregate value of products	
	1900	1905	1900	1905
New York City	19,243	20,839	$1,172,870,261	$1,526,523,006
Yonkers	107	105	17,303,690	33,548,088
Metropolitan District in N. Y.	19,350	20,944	$1,190,173,951	$1,560,071,094
State of N. Y.	35,957	37,194	$1,871,830,872	$2,488,345,579
Bayonne	63	58	$38,601,429	$60,633,761
Bloomfield	39	33	3,370,924	4,645,483
Elizabeth	141	124	22,861,375	29,300,801
Hackensack	21	23	782,232	1,488,358
Harrison	41	41	6,086,477	8,408,924
Hoboken	194	279	10,483,079	14,077,305
Jersey City	536	628	72,929,690	75,740,934
Kearney	16	11	1,607,002	4,427,904
Montclair	23	19	663,592	621,145
Newark	1,573	1,600	112,728,045	150,055,227
Orange	74	66	2,995,688	6,150,635
East Orange	22	17	2,086,910	2,326,552
Passaic	70	95	12,804,805	22,782,725
Paterson	487	513	48,502,044	54,673,083
Perth Amboy	47	53	14,061,072	34,800,402
Union	57	77	3,403,136	3,512,451
West Hoboken	65	95	4,769,436	5,947,267
Metropolitan District in N. J.	3,469	3,732	$358,736,936	$479,592,957
State of N. J.	6,415	7,010	553,005,684	774,369,025
Total of U. S.	207,562	216,262	$11,411,121,122	$14,802,147,087

Summary.

	Establishments.		Aggregate value of products.	
	1900	1905.	1900.	1905.
Metropolitan District, N. Y.	19,350	20,944	$1,190,173,951	$1,560,071,094
Metropolitan District, N. J.	3,501	3,781	361,174,370	483,165,091
Metropolitan District, Total.	22,851	24,725	1,551,348,321	2,043,236,185
Remainder of United States.	184,711	191,537	9,859,772,801	12,758,910,902
Total of U. S.	207,562	216,262	$11,411,121,122	$14,802,147,087

From the preceding tables it will be seen that the States of New York and New Jersey, which contain about one-eighth of the population of the United States, produce within their bounds nearly a quarter of the aggregate national manufactures. Of the three and a quarter billions made in these two States, about two billions fall to the share of the Metropolitan District, or about one-seventh of the entire production of the United States, while its population may be estimated at about one-twelfth of the total. The importance of the District as a factor in our national industrial economy is thus amply illustrated. With its two-billion annual product of varied manufactures, the Metropolitan District far outstrips the other general manufacturing cities in the country, Chicago being next in importance, with one billion dollars, Philadelphia and Camden following with six hundred and twenty-five million, and Boston with the neighboring cities showing about three hundred and sixty millions.

The manufacturing capital in the whole of the United States was, in 1905, about thirteen billion dollars, or 86 per cent. of the annual product. The proportion shown for the Metropolitan District was about 72 per cent. of the annual product. Thus the Metropolitan District gets a larger return on capital invested than the rest of the country.

COST OF LABOR.

By the Census figures, the amount of wages paid in the entire country on the product of $14,802,000,000 in 1905 was $2,611,000,000, or about 18 per cent. The separate figure for the Metropolitan District was about 16 per cent. This again can be attributed to power plants and high value of machine output.

The author concludes by expressing the belief that the territory thus described and recognized as the great Metropolitan District is destined to become the most interesting technological center in the world and the seat of the most varied and the largest establishments in the country treating raw materials for the production of staples.

Some Experiments on the Case Hardening of Steel with Gases.

By J. C. Olsen and John S. Weiffenback

This paper gives the results of experiments on case hardening of soft Norwegian iron with various gases, carried on at the Polytechnic Institute. It was shown that in most cases nitrogen in the form of ammonia facilitates the action of carbonizing gases. Nitrogen in the free state has no influence on the carbonizing action. It was shown that the ammonia does not react with the carbon gases to form cyanogen. Carbon monoxide seems to act almost as well without as with ammonia. The depth to which the carbon penetrates and the percentage of carbon in the case were determined by analysis. The chemical reactions taking place during the carbonization were determined as follows:

With carbon monoxide $2CO = C + CO_2$

With methane $CH_4 = C + 2H_2$.

With acetylene two reactions seem to take place, as follows:

$$2C_2H_2 = CH_4 + 3C$$

and

$$C_2H_2 = C_2 + H_2.$$

The carbonizing ability of the gases studied ranges according to the following order: Carbon monoxide, acetylene, illuminating gas, methane. Carbon monoxide is by far the best gas for this purpose.

NATIONAL FERTILIZER ASSOCIATION.

Sixteenth Annual Convention, Atlantic City, N. J., July 6 and 7, 1909.

Preliminary Report of the Committee on the Analysis of Phosphate Rock.

Last October, this committee gave out its first report[1] of the work done in 1908. In this, we tentatively recommended and came to the following decision:

"That for referee work, the official gravimetric method be used for phosphoric acid, and that in the methods now in use for iron and alumina, the solvent be hydrochloric acid (1:1) until the question of the effect of pyritic iron in acidulating can be definitely solved. The methods for iron and alumina will be investigated further with a view to the adoption of one of the methods as standard for our work.

"We believe that a strict adherence to uniform details in these methods will yield very much better results and that it is essential for our fertilizer chemists to agree upon these details. We are, therefore, preparing a set of methods to include moisture, the official gravimetric and volumetric methods for phosphoric acid, and the various methods for iron and alumina, which will give complete details as far as possible. These methods will be submitted to all the chemists who previously worked on the samples with the request that the work be gone over again, following in detail, the instructions given."

On April 5, 1909, a new standard sample of phosphate rock together with uniform methods of analysis based upon results of correspondence and comments of last year's work by coöperating chemists, were sent out to nearly fifty chemists. Reports were rather slow coming in, however, and on June 3rd, a letter was sent out requesting a prompt report of results. To date, reports from twenty, or less than half of the chemists to whom samples were sent, have been received, and a full report cannot, therefore, be presented.

In comparing the results obtained so far this year with the results obtained last year, it must be borne in mind that the number of results from last year is over six times as great as this year, due to the fact that four samples were sent out last year and all of the results are in, whereas, only one sample was sent out this year and less than half of the results are in.

The results reported on moisture showed no improvement over those of last year. The extreme variations were fully as wide and as many as last year. In both cases, approximately 60 per cent. of the results agreed with each other to within 0.2 per cent.

The results on phosphoric acid by the gravimetric method showed a marked improvement. Last year 53 per cent. of the results agreed to within less than 1 per cent. calcium phosphate; this year 60 per cent. of the results agree to within 1 per cent. calcium phosphate. As a matter of fact, the results included in this 60 per cent. agree with each other to within about 0.7 per cent. calcium phosphate.

The results on phosphoric acid by the volumetric method show an immense improvement over those of last year.

[1] This Journal, 1, 41.

Last year only 28 per cent. of the results reported agreed to within 1 per cent. calcium phosphate; this year, 70 per cent. agree to within 1 per cent. calcium phosphate. As a matter of fact, the results included in this 70 per cent. agree with each other to within less than 0.5 per cent. calcium phosphate.

Another marked improvement is in the even closer agreement of the averages of phosphoric acid by the volumetric and gravimetric methods. Last year the averages differed by 0.05 to 0.17 per cent. phosphoric acid; this year, the averages are practically identical, omitting, of course, from the averages the widest variations.

The results obtained by other methods than those sent out are few in number and need not be mentioned now, except that some of them are of very great interest because of their close agreement with the averages obtained by the methods sent out.

The results of iron and alumina by the caustic potash method also showed a marked improvement. Last year only 35 per cent. of the results agreed with each other to within 0.2 per cent., whereas this year 46 per cent. showed as good an agreement as this. The extreme variations were not nearly as wide as those last year. It should be stated that these figures include the results of last year by both the Smith or modified Von Grueber and the Gladding methods, which are nearly alike and correspond practically to the caustic potash method sent out this year.

The results of iron and alumina by the acetate method vary too widely to admit of comparison as made above. The variations last year by the acetate and Wyatt methods, which are similar, were very great and the results were entirely unsatisfactory. The results reported this year on the acetate method vary just as widely, but it is interesting to note that 50 per cent. of the analyses reporting on the method this year get results agreeing to within about 0.4 per cent. and that the averages of these results agree with the average of the caustic potash results to within less than 0.2 per cent.

It is gratifying to note the general improvement in the agreement of results, but there is still much room for further improvement.

Definite recommendations cannot be made until the results are practically all in. As soon as all the results have been received, they will be tabulated and the recommendations of this committee will be based on the outcome of these results. We had hoped to be able to make quite definite recommendations as to standard methods to be adopted by this Association, but it seems at the present time that standard methods alone are not enough to insure uniformity. From the results it has become evident that considerable familiarity and experience with any method is required before dependable results can be obtained by it. For this reason it seems that standard methods will have to be accompanied by standard samples so that every interested chemist can obtain such standard samples with which to verify his work by any given method from time to time.

We propose to go right ahead with this work, continuing same until we have found a complete method which will give the best results in the hands of the largest number of analysts. At the last meeting of the American Chemical Society, there was formed a Fertilizer Division, of which Dr. Carpenter, one of the members of this committee, is chairman. This Division has committees working on methods of fertilizer analysis, and we have been invited to coöperate with these committees in this work. Inasmuch as most of our chemists are members of this Fertilizer Division, we recommend that we continue this work through this Fertilizer Division of the American Chemical Society. By doing this we believe that we can get quicker results, and that, because of the increased backing this work will have, we will secure the recognition and coöperation of the official state chemists.

C. H. Dempwolf, Jr.,
F. B. Carpenter,
C. F. Hagedorn.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, 908 G Street, N. W., Washington, D. C.

917,129. Manufacture of Hydraulic Cement. Charles J. Potter, Willington Quay, England. April 6, 1909.

The cement is made by burning a mixture of calcareous matter, clay and silica, all almost free from iron, with fuel almost free from iron, and then cooling the resulting clinker in a reducing atmosphere.

917,176. Method of Recovering Metals. Walter O. Snelling, Pittsburg, Pa. April 6, 1909.

This is a method of recovering metals from their compounds by disposing such compounds in connection with an electrode in a suitable electrolytic bath and reducing portions of the compound to metal, and thereafter connecting said metal as anode in said bath to dissolve the reduced metal and re-deposit the same.

917,191. Process for Obtaining Radioactive Bodies from Uranium or Thorium, etc. Adriaan P. H. Trivelli, Scheveningen, Netherlands. April 6, 1909.

This is a process for producing radioactive bodies from uranium, thorium or from their compounds, simultaneously exposing uranium, thorium or their compounds, *in vacuo*, to the action of cathode rays and of radioactive bodies.

917,265. Preserving Wood and the Like. Bernard Diamand, Idaweiche, Oberschlesien, Germany. April 6, 1909.

The process of impregnating wood and the like, which consists in filling a vessel with the wood and impregnating fluid to displace the air therein, partially withdrawing the fluid while preventing the admission of air to produce a vacuum, and then reintroducing the fluid under pressure.

917,285. Manufacture of Aluminum-foil. Alfred Gautschi, Gontenschwil, Switzerland. April 6, 1909.

The process consists in rolling as a packet, sheets of pure aluminum folded a number of times upon themselves, the surfaces of the sheets in contact one with the other being always coated with a solution of oil and water, the rolling being effected between heated cylinders.

917,475. Direct Process of Manufacturing Iron and Steel. Thomas J. Heskett, Brunswick, and Montague Moore, Melbourne, Victoria, Australia. April 6, 1909.

The process consists in forming the slag over the reduced metal within a furnace, the slag being kept in a ferrous condition by the mixture therewith of reduced iron and a reducing substance.

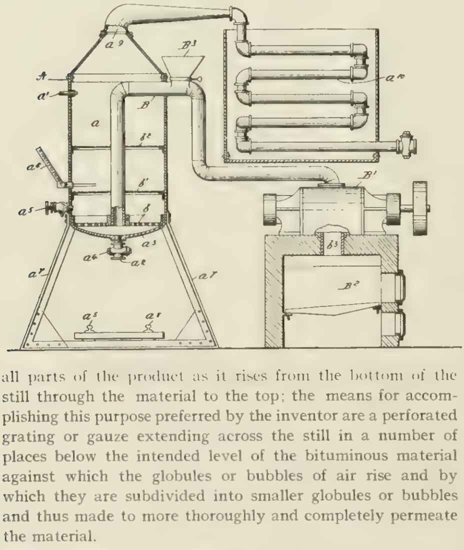
917,502. Process of Making Phosphoric Acid and Glauber Salt. EMERSON H. STRICKLER, New York, N. Y. April 6, 1909.

The process consists in separating Glauber salt and phosphoric acid in the solution obtained by the digestion of phosphate rock in bisulphate of soda solution in combining proportions, by causing the Glauber salt to crystallize from the phosphoric acid by concentrating and cooling.

917,702. Still for Distilling Crude Bituminous Products. HORACE W. ASH, Cambridge, Mass. April 6, 1909.

This still is particularly intended for distilling bituminous material for the purpose of producing a refined bituminous product especially adapted for use in the manufacture of bituminous pavements. The bituminous material which it is intended to use for obtaining this product is a crude tar obtained from gas works and petroleum oils having an asphalt base.

The still is so constructed that the bituminous material therein may be subjected to a volume of heated air or steam introduced into the bottom of the still whereby the material is not only heated, but is aerated by the passage through it of large quantities of air in the form of small globules or bubbles. Means are provided in the still whereby the air is disseminated and brought into intimate relation with



all parts of the product as it rises from the bottom of the still through the material to the top; the means for accomplishing this purpose preferred by the inventor are a perforated grating or gauze extending across the still in a number of places below the intended level of the bituminous material against which the globules or bubbles of air rise and by which they are subdivided into smaller globules or bubbles and thus made to more thoroughly and completely permeate the material.

917,707. Process of Making Carbid or Carbid-containing Electrodes. HENRY S. BLACKMORE, Mount Vernon, N. Y. April 6, 1909.

This is a process of making a composite carbid electrode by mixing a metal carbid with a solid hydrocarbon carbon-yielding compound and exposing the composition to the action of heat sufficient to dissociate the carbon-yielding substance.

917,787. Process of Making Storage-battery Plates. WILLIAM MORRISON, Chicago, Ill. April, 13 1909.

The process consists in mixing a suitable quantity of soft lead and an oxid of lead, and in then reducing the same to paste form by adding a liquid preparation obtained by mixing together water and acetone, sulfate of ammonia and acetic acid.

918,025. Process of Burning Cement Clinker. CARLETON ELLIS, White Plains, N. Y. April 13, 1909.

This is a process of burning cement material in inclined rotary kilns, which consists in spreading the cement material over the upturning side of the kiln to a point within one of the upper quadrants of the kiln, projecting against and along the material so spread a flame jet which in cross-section is broad in one direction and thin in a direction at right angles, the broad side of the flame turned toward the cement material so spread out, and causing the material on the upper edge of the layer of cement material to shower down through said flame.

918,269. Process of Producing Metals. HENRY S. BLACKMORE, Mount Vernon, N. Y. April 13, 1909.

This is a process of producing metal, which consists in exposing a substance, containing a metal and oxygen, capable of reacting with a carbid to yield metal, to electrolysis, while employing an electrode containing calcium carbid.

918,381. Metallurgy of Iron. WILLIAM S. SIMPSON and HOWARD OVIATT, London, England. April 13, 1909.

This is a process of producing iron directly from the ore which involves mixing the ore in a fine state of division with a carbohydrate associated with water, and subjecting the same to heat to effect the reduction of the metallic oxids.

918,382. Metallurgy of Steel. WILLIAM S. SIMPSON and HOWARD OVIATT, London, England. April 13, 1909.

The process consists in manufacturing steel directly from ore by reducing the ore by means of a carbohydrate and effecting carburization of the metal by means of another form of carbon at the same operation.

918,384. Waterproof Cement. MELVILLE M. SMITH, Fredonia, Kansas. April 13, 1909.

The invention consists in a process of making white waterproof cement, by the admixture of lime and clay as free as possible from iron, together with a flux, burning the resulting mass to the verge of fusion, that is to say, beyond the sintering limit, and grinding the resulting clinker with a mixture of clay free from iron.

918,419. Process for Producing Carbids. REMO CATANI, Rome, Italy. April 13, 1909.

This is a process of making calcium carbid compounds by coating the carbon with slaked lime and heating such coated carbon and also slaked lime into an electric furnace, the electrodes in the furnace being also coated with slaked lime.

918,424. Process of Purifying Smelter-gases. PAUL DANCKWARDT, Denver, Colo. April 13, 1909.

The process consists in eliminating the destructive in-

gredients from smelter gases, by passing the gases together with steam through a body of glowing carbon, and mixing the resulting gases with further quantities of the original gas-containing sulphur dioxide, after which the gases are brought in contact with a solution containing some metallic salt which will not react with the gases, cooled, and again washed with a solution of an iron salt.

918,647. **Treating Anode Slime from the Electrolytic Refining of Lead.** ANSON G. BETTS, Troy, N. Y. April 20, 1909.

The process consists in treating anode slime from the electrolytic refining of lead by dissolving metal therefrom by treatment with a solution containing fluorin ion, and with an oxidizing agent, of which the products of reduction by the slime are soluble in the solution, the said solution also containing a strong acid forming a soluble lead salt, and recovering metal of the slime from the resulting solution.

918,648. **Process of Smelting Zinc Ores.** ANSON G. BETTS, Troy, N. Y. April 20, 1909.

The process consists in treating zinc ore by mixing the ore with a reducing agent unoxidizable by air below a temperature of 800° C., heating the mixed ore and reducing agent by the heat of a combustion process and reducing the ore by the action of said reducing agent at a higher temperature.

918,908. **Process of Extracting Silver from its Ores.** JAMES C. PRYOR, North Bay, Ontario, Canada. April 20, 1909.

The method consists in eliminating the baser metals from an ore containing silver with baser metals, by first calcining the ore to oxidize the metals therein; then treating the oxidized ore with a suitable reagent to reduce the oxids so formed; then treating the mass with a solvent of the baser metals.

918,925. **Process of Treating Starch.** FREDERICK SUPF, New York, N. Y. April 30, 1909.

This is a process for rendering starch capable of swelling in cold water by treating the starch with a suitable solution of a sulfocyanate, and then washing the same with a suitable solvent.

918,950. **Process of Reducing Metal.** HENRY S. BLACKMORE, Mount Vernon, N. Y. April 20, 1909.

The process consists in exposing a substance containing metal to electrolysis, while employing an electrode containing a metal acetylid decomposable by an ingredient of the substance employed and capable of liberating therefrom.

918,997. **Process for Producing, from Straw, a Liquid Suitable for the Production of Alcohol.** WILLIAM F. GILES, New York, N. Y. April 20, 1909.

This is a process of producing a liquid for the production of alcohol by leaching out successively separate quantities of straw under pressure with the same quantity of boiling water, removing the concentrated liquid thus obtained, acidulating the same and allowing it to rest whereby the extracted substances are transformed into fermentable matter.

919,031. **Process for Rendering Material of Any Kind Proof against the Action of Moisture and of Chemical Agents.** ABRAHAM KRONSTEIN, Karlsruhe, Germany. April 20, 1909.

The process consists in impregnating the material with liquid wood oil (tung oil) and subjecting the material thus containing the oil to a temperature sufficient to convert the oil into its solid polymeric form.

919,049. **Process of Purifying Potassium Bitartrate.** MANUEL F. MARTINEZ, Jerez de la Frontera, Spain. April 20, 1909.

The process consists in treating crude tartar with a mineral acid in the cold state, filtering and decolorizing the resulting liquid, treating said liquid with an alkaline salt, precipitating the metallic compounds in the solution, filtering the solution, then adding a potash salt to the filtered solution to precipitate bitartrate of potassium.

919,165. **Electric Smelting-furnace.** HERBERT CHAMPION HARRISON, Exton, Pa. April 20, 1909.

This invention consists in a furnace of the arc type and a method of operating the same, employing polyphase cur-

Fig. 1.

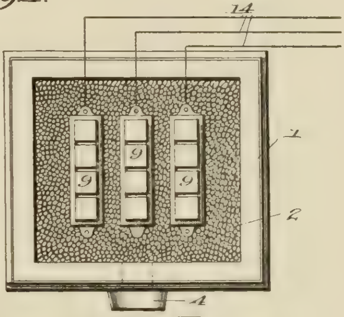


Fig. 2.

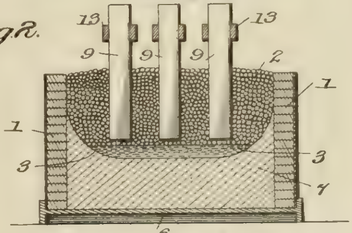
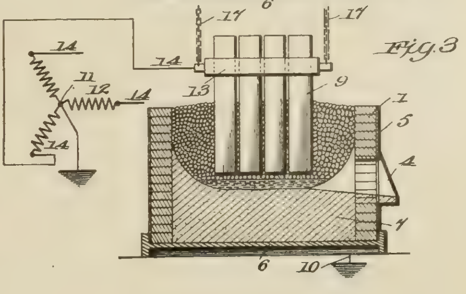


Fig. 3.



rents for the purpose of smelting the charge, and using reducing agents, whereby the products of reduction are obtained continuously in the form required by tapping the same.

The structure of the furnace and the electrical connections thereof will be obvious from the illustration. The process consists in vertically disposing arc electrodes in the furnace; in connecting each electrode to one of the branches of the star connection of a polyphase generator; in so spacing the electrodes that a single bath is formed and an arc between each electrode and said bath is also formed; and in placing resisting charge material between said electrodes to prevent any substantial leakage of current from electrode to electrode.

919,434. Process of Extracting Precious Metals from Their Ores. WILLIAM L. IMLAY, Conestoga, Pa. April 27, 1909.

The process consists in continuously conveying them through successive bodies of cyanid solution, and alternately heating, cooling and agitating said ore and solution while exposed to the action of light and air.

919,839. Process of Removing and Recovering Tin. JULIUS ELKES, Mount Pleasant, Pa. April 27, 1909.

This is a process of recovering tin from old and scrap materials, by converting the tin into a tin sulphid, then converting it into a tin dioxid and then reducing the tin dioxid with coal.

920,119. Manufacture of Fuse. HENRY E. ELLSWORTH, Simsbury, Conn. May 4, 1909.

The method comprises the treating of strands of threads with a fire-proofing solution, spinning the strands, and feeding a medium for conveying the fire into the strands as they are being spun.

920,224. Process of Manufacturing Nitric Acid. FRIEDRICH S. VALENTINER, Leipzig-Plagwitz, Germany. May 4, 1909.

The process consists in creating an excess of pressure in a retort containing sodium nitrate and sulphuric acid by throttling the nitric acid gases passing from the retort, maintaining a partial vacuum in the condenser, and purifying the collecting condensate by forcing these through the following uncondensed nitric acid gases.

920,332. Method of Manufacturing Sublimed White Lead. LOUIS S. HUGHES, Joplin, Mo. May 4, 1909.

The process consists in treating ores or compounds containing lead sulphid for the production of sublimed white lead, a product consisting chiefly of lead sulphate, without the production of metal, slag, or other fused or liquid product, by finely dividing the ore or compound, mixing it with air, igniting the mixture of air and ore particles, maintaining its combustion at temperatures below those at which the ore particles will fuse, separating the unburned particles of ore from the gases and lead sulphate fume by subsidence and separating the lead sulphate from the gases.

920,335. Method of Manufacturing Litharge. LOUIS S. HUGHES, Joplin, Mo. May 4, 1909.

The process consists in finely dividing the carbonate, maintaining a furnace at a temperature sufficient to decompose the carbonate into litharge and carbonic acid and with a substantially non-reducing atmosphere, injecting the finely divided carbonate into the heated portion of the furnace and separating the litharge from impurities.

920,391. Process for Refining Metal. JAMES H. REID, Newark, N. J. May 4, 1909.

The process consists in reducing and refining metal ore by first melting the ore, then mixing the same with carbon monoxid gas to produce a frothy mass of gas and ore, and then rotating said mass and exhausting the surface thereof.

920,560. Manufacture of Iron or Steel by the Basic Bessemer Process. JOSY FLOHR, Rodange, Luxemburg. May 4, 1909.

The process consists in blowing air through molten pig iron contained in a converter, until the carbon is wholly or almost wholly burned, and then introducing calcium hydrate briquets into the bath and again blowing in air until the refining operation is completed.

920,601. Process of Making Metal Sulphates. OTTO MEURER, Cologne, Germany. May 4, 1909.

The process consists in first heating the sulphids with alkali sulphid, then exposing the mass to air until self-oxidation has proceeded only so far that the ferric oxide produced remains soluble in dilute acid, and finally lixiviating the mass.

920,610. Process and Apparatus for Producing Oxids of Nitrogen by Means of a Rotary Flame. IGNACY MOSCICKI, Freiburg, Switzerland. May 4, 1909.

The process consists in maintaining electrically a flame between the electrodes; interposing auxiliary cooling gases between the electrodes to increase the resistance and prevent short-circuiting and introducing reaction gases to the influence of said flame.

920,638. Process for Diminishing the Formation of Flaws or Blow-holes when Casting Blocks and Other Pieces. ALFRED VON PARAVICINI, Hagen, Westphalia, Germany. May 4, 1909.

This is a method of diminishing the formation of flaws or blow-holes in the casting of blocks and other pieces by covering the surface of the feeding head with a bottom layer of solid incombustible material in a state of division which is substantially inert with relation to the metal to be cast and with a top layer of a combustible substance likewise in state of division.

920,828. Process of Making a Cellulose Material. CHARLES F. GROSS and JOHN F. BRIGGS, London, England. May 4. 1909.

The process consists in treating fibrous cellulose with an appropriate acetylating agent until there is an increase in its weight not exceeding 50 per cent., without appreciable alteration of the textile qualities of the fiber.

921,975. Process of Obtaining Nitric Acid from Gas Mixtures Containing Oxids of Nitrogen. LUDWIG GLASER, Berlin, Germany.

The process includes the steps of absorbing the nitric oxid by means of a weak basic oxid, and subsequently heating to a high temperature to drive out the nitric oxid in concentrated form.

922,003. Process of Making Ammonia. CONSTANTIN KRAUSS, Westergein, Germany. May 18, 1909.

The process consists in producing ammonia from suitable cyanogen compounds by subjecting a mixture of the same with chloride of calcium to the action of water and heat.

922,031. Method of Making Sodium Sulphate. JOHN D. PENNOCK, Syracuse, N. Y. May 18, 1909.

The method consists in mixing niter cake and a sodium compound, having an alkaline reaction, in approximately reacting proportions, then effecting a reaction between the acid and alkaline components and recovering the resulting sodium sulphate.

922,088. Process of Removing Sulphur, Arsenic and Other Like Impurities from Refractory Ores. FRANK COTTON, Hornsby, New South Wales, Australia. May 18, 1909.

This is a process for the preparation of auriferous and argentiferous refractory ores contaminated with impurities such as sulphur, arsenic, antimony, zinc and the like, consisting in the removal of the sulphur by the action upon the heated ore of free hydrogen under slight pressure, the subsequent oxidation of the base metals capable of oxidation present in the desulphurized ore by the action of steam upon the same, and the final driving off by heat from the desulphurized and oxidized ore of the remaining volatile oxids present.

922,340. Manufacture of Objects from Cellulose Acetate. ALBERT SCHLOSS, Stettin, Germany. May 18, 1909.

The process comprises the subjection of the cellulose acetate to the action of formic acid as a solvent and the introduction of the solution so formed into an aqueous precipitating bath.

922,369. Process of Extracting Resin and Turpentine. GEORGE WALKER, New York, N. Y. May 18, 1909.

The process comprises distilling off volatile bodies from a resinous wood at a temperature insufficient to injure the rosin, and subsequently extracting the wood with a neutral volatile solvent to remove rosin.

922,388. Process of Making Ferro-nickel and Nickel-steel. FRANKLIN R. CARPENTER, Denver, Colo. May 18, 1909.

The method consists in freeing sulphid copper-nickel-iron ores from their copper contents by oxidizing the nickel and iron sulphids and then chloridizing the copper sulphid, leaving the nickel and iron oxids in the form of the purple ore of commerce.

922,409. Process of Recovering Hydrocyanic Acid. WALTHER FELD, Honningen-on-the-Rhine, Germany. May 18, 1909.

The process consists in obtaining hydrocyanic acid from metallic cyanids in a solid state by subjecting the latter at a temperature above 100° C. and in the presence of steam to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

INDUSTRIAL AND TRADE NOTES.

Mining and Minerals—Canada.

(*Concluded from p. 326.*)

Corundum, tons	1,039	100,389
Feldspar, tons	7,877	21,099
Graphite, tons	251	5,565
Grindstones, tons	3,843	45,128
Gypsum, tons	340,964	575,701
Limestone for flux, in iron furnace, tons	418,661	289,705
Magnesite, tons	120	840
Mica	......	191,602
Barytes, tons	4,091	18,265
Ochers, tons	4,746	30,440
Mineral waters	......	109,391
Natural gas	.....	1,012,060
Petroleum, barrels	527,987	747,100
Phosphate (apatite), tons	1,596	14,794
Pyrites, tons	47,336	224,824
Quartz, tons	27,134	32,277
Salt, tons	79,975	378,798
Talc, tons	276	3,048
Tripplite, tons	30	197
Total	......	$32,479,006

Structural Material and Clay Products

Classification.	Quantity.	Value.
Cement, natural, barrels	1,044	$ 815
Cement, Portland, barrels	2,655,289	3,709,063
Flagstones	4,000	3,600
Sand and gravel (exports), tons	298,954	161,387
Sewer pipe	....	514,042
Clay products, stone, lime, etc (estimated)	.....	8,500,000
Total	....	$12,888,907
All other nonmetallic	......	32,479,006
Total value, nonmetallic	.....	$45,367,913
Total value, metallic	..	41,655,936
Mineral products not reported	....	300,000
Total value, 1908	...	$87,323,849

—*U. S. Consular Report*, April 12, 1909.

Nonmetallic Products

Classification.	Quantity	Value
Arsenic, tons	699	38,054
Asbestos, tons	65,534	2,547,507
Asbestic and asbestic sand, tons	25,239	25,829
Calcium carbide, tons	6,864	417,150
Chromite, tons	7,225	82,008
Coal, tons	10,904,466	25,567,235

Responding to instructions, Consul-General R. E. Mansfield, of Zurich, has investigated and prepared the following account of the operations in Switzerland of the modern method of making liquid gas and of its utilization:

While the principle of producing liquid gas was discovered nearly a century ago, and such chemists as Faraday (1823), Andrews (1861), and scientific investigators like Cailletet, of Paris, and Pictet, of Geneva (1877), left valuable records relating to the subject, they succeeded in establishing only a theory that "all gases pass into a liquid condition, provided that they are submitted to a sufficiently low temperature and to a sufficiently high pressure."

The first plant for the manufacture of liquid gas as a com-

mercial commodity was established in Augsburg, Bavaria, in 1904, under a process invented by Herr Blau.

In 1907 a stock company for the manufacture of liquid gas was organized in Zurich, under the name of the "Swiss Liquid Gas Company" (Schweizer Fluessig-Gas-Fabrik, L. Wolf, A. G.), and a factory, with a capacity of 480 pounds of liquid gas a day, was established at Bassersdorf, near Zurich. The apparatus for the purpose of transforming crude oil into liquid gas, with which the factory is equipped, is the invention of L. Wolf, a resident of the village of Bassersdorf. The product is described by the company as "a transportable liquid, which is simply evaporated as used, and can be used for lighting, heating, cooking, soldering, and welding purposes."

The factory building is a plain one-story stone structure, 40 by 72 feet, and was built at a cost of $24,000. It is equipped with one 12-horse-power explosion gas engine, which furnishes the motive power to drive the compressors working at high speed. The engine is supplied with gas produced in the process of reducing the crude oil to liquid gas. The furnaces in which the retorts are heated are also partially supplied from the same source, about one-half of the fuel consuming being surplus or exhaust gas. The application of this by-product reduces the cost of fuel for operating the plant to the minimum. In addition to the residue of gas, a considerable residuum of tar is secured in the process. From the tar may be extracted lubricating oils, benzole, creosote, and materials suitable for street and road dressing as a dust preventive.

The material from which the liquid oil is produced in the Bassersdorf factory is the residue or refuse of crude oil after various ingredients, such as benzine, vaseline, etc., have been extracted. It is imported from Austria. At the factory, the crude oil is transferred from a reservoir into the retorts by an automatic process. The cost of the oil used in the Swiss company's factory is about 7 cents per gallon.

After passing through the process of heating, condensation, and cooling, and the various carbonizing and other substances have been separated from it, the liquid gas is placed in steel tubes of various sizes, holding 20, 40, 60 and 80 pounds each, in which form it is ready for use. The tubes containing the material are accepted by the railways and other carrying companies without restrictions or special provisions, as the gas is nonpoisonous and is three times less explosive than ordinary gas. The liquid gas is utilized by attaching one of the tubes to the special apparatus manufactured by the company, which contains a regulator, gage, etc.

The Bassersdorf concern, which has passed beyond the experimental stage, now has over 100 installations in different towns and cities in Switzerland, all of which are declared to be entirely satisfactory to the purchasers. In a descriptive circular regarding the production of liquid gas, its uses, etc., the company says:

The liquid gas is obtained by the dry distillation of raw petroleum and of by products of the lignite and oil industries. The raw materials are decomposed in retorts by the action of a high temperature; the vapors and gases produced then pass through the tar separators and the cleaner, losing here the easily condensable gases (tar, benzine, etc.), as well as any deleterious and malodorous byproducts that may be present. By means of Wolf's patent apparatus, and the use of cold and pressure, a separation of the difficultly liquefiable gases, such as hydrogen, methane, etc., from the more liquefiable ethane, propane, pentane, etc., is obtained. These are then liquefied, carburetted, and filled into steel transport cylinders provided with a valve and sold as "liquid gas." It is easily transportable and utilizable and has a high illuminating and heating power. The prime cost is not greater than that of other kinds of gas produced in small plants. The installation costs are low and the manipulation is simple and without danger. The gases not liquefied are used in the working of the factory.

It is claimed for the liquid gas that it is nonpoisonous, and its explosiveness is about three times less than coal gas.

Specific gravity of the liquid gas (water = 1), about	0.568
Specific gravity of gaseous liquid gas (air = 1), about	1.021
1 liter gaseous liquid gas weighs (at 0° and 760 mm pressure), g.	1.3201
1 cubic meter (35.314 cubic feet) liquid gas weighs under like conditions, kilos	1.3201
Maximum heating value per cubic meter of gas (at 0° and 760 mm. pressure), thermal units	16.046
Minimum heating value per cubic meter of gas (at 0° and 760 mm press re) thermal units	15.137

The company's descriptive circular says:

The liquid-gas installation consists of the transportable cylinder containing the liquid gas, of a gas tank fitted with a pressure gage and an adjustable safety valve; also of a regulator for adjusting the pressure of the gas.

The advantages and conveniences offered by liquid gas presents for it a wide field of usefulness. Among the various uses to which it may be applied are the heating and lighting of residences, public buildings, hotels, and manufactories, and street lighting and cooking purposes; also chemical and technical laboratories, soldering, and welding. If mixed with oxygen, it produces a heat so intense that an ordinary bar of iron 1 inch in diameter can be cut in two almost instantly by placing it in the flame of a liquid-gas burner. This concentrated heating power makes it available, and especially desirable in the smelting and forging of iron and steel.

Concerning its application as a means of welding, etc., the company claims for liquid gas that:

Any required grade of heat favorable for the metal to be welded can be produced by simply regulating the pressure and quantity of gas. The metal melts and flows together without oxidizing; no pressing, no hammering, is necessary, and the metal does not turn brittle. With a medium heating value of 15,600 thermal units, liquid gas affords the cheapest and best method for the welding of metals.

The success of the Bassersdorf factory has demonstrated the fact that liquid gas can be manufactured and sold at a profit in competition with coal gas and electricity, as nearly every town and village in Switzerland is supplied with artificial-gas works and an electric-lighting plant. Yet within a short space of time, the company has placed over 100 liquid-gas installations, and the demand for its product keeps the plant running full capacity day and night. When it is understood that the factory was built more as an experiment and for the purpose of demonstrating the practicability of manufacturing liquid gas as a material for heating and lighting than as a commercial enterprise, and the fact that all the material used is imported, which greatly increases the cost of production, it can be readily seen that greater profits might be obtained from the manufacture in the United States, where raw material, such as waste from rock-oil refineries or other kind of bituminous oils, are plentiful and comparatively cheap.

The Zurich company, which possesses international

patents, has disposed of the rights to manufacture under its process in France, and a plant with a capacity of 1,056 pounds of liquid gas per day is in course of construction in Paris and will soon be ready to begin operations. A factory equipped with the Wolf patent apparatus is being built in Boston.

The Swiss plant turns out 480 pounds of liquid gas per day, besides a considerable quantity of tar. Only 4 men are employed in the work of operating the factory, which runs day and night. No special mechanical skill is required in the work, which reduces the cost of labor to the minimum. For the construction and installation of plants for lighting, heating, cooking, industrial, and laboratory purposes about 20 mechanics are employed. These men also act as soliciting and selling agents and promoters of the company's interests in towns where there are no coal-gas plants.

The finished product is put up in different-sized metal tubes, holding 20, 40, and 80 pounds each, the market price being 15 cents per pound, or $3 for a tube containing 20 pounds. This gives the daily output of the factory, amounting to 480 pounds, a total value of $72.

ESTIMATED COST OF PRODUCTION AND PROFITS.

The Zurich company estimates the cost of production, profit, etc., on a plant with a capacity of 44 pounds of liquid gas per hour, as follows:

Forty four pounds per hour, 1,056 a day, for 300 days in the year, 316,800 pounds, market value, 15 cents per pound		$47,520.00
Cost of production: Raw material gas oil, 2,240 pounds daily, or 672,000 pounds for the year, at a cost of 0.724 of 1 cent per pound	$4,825.28	
Carburetting: 422 pounds daily, 126,600 pounds for the year, at 38.6 cents per pound	4,876.66	
Fuel: 1,815 pounds daily, 544,500 pounds per year, at 3 cents per pound	1,633.50	
Wages and salaries:		
Four workmen, at $1 16 per day each, for 300 days	1,392.00	
One foreman	695.00	
One clerk	465.00	
Total cost per year		13,927.44
Profits for 1 year		33,592.56

Estimated cost of building a liquid gas factory with a capacity for producing 1,056 pounds per day, $5,000. Cost of machinery and apparatus for operating the plant, $40,000.

Renewed efforts are being made to establish a fertilizer combination. Immediately following the abandonment of the earlier product which contemplated bringing about 50 manufacturers into one combination capitalized at $50,000,000, certain interests began working upon another basis to effect the same result. Efforts have progressed so far that the new company has been incorporated and its organization completed.

The new company was chartered on June 24th under the laws of New York with a nominal capital of $1,000. This will be increased to $15,000,000, half common and half 7 per cent. cumulative preferred. At present the company comprises the Buffalo Fertilizer Co. owned by Thomas C. Meadows, and large potash interests in Germany belonging to Waldemar Schmidtman, both of whom were in the earlier enterprise. It is the intention, however, to add extensively to the company's holdings. The name of the new company will be the International Agricultural Corporation. Schmidtman will probably be president and Meadows vice-president.

Among the assets of the old company which it is expected that the new concern will take over, is a contract for the sulphuric acid output of the Tennessee Copper Co. This contract involved the payment to the copper company of $1,000,000, of which about $750,000, it is said, was paid over when the fertilizer consideration fell through. Of this sum, Mr. Schmidtman put up $150,000 and Mr. Meadows, $100,000.

Consul-General George E. Anderson, of Rio de Janeiro, reports as follows concerning the iron and manganese ore deposits of Brazil:

The Brazilian Government has just transmitted a report, for the use of the authorities having in charge the preliminary preparations for the International Geological Congress, which meets next year in Stockholm, covering certain iron-ore deposits in the Republic, the result of a survey sent out for the purpose, with a special expert at its head; and although the text of this report is withheld, pending the use to be made thereof by the authorities for whom it was prepared, enough of it has been secured by this office to predict that it will startle the iron world and be the sensation of the congress.

The examination of the deposits in Minas Geraes located 52 outcroppings of ore which was from 60 to 75 per cent. pure iron, free from all impurities which might interfere with its proper smelting. Of these outcroppings, the expert selected 9, of average size and quality, which he carefully surveyed and measured, calculating their contents at a little less than 1,000,000,000 tons of very high-grade ore, on or near the surface and in situations permitting easy working and economical handling. On the basis of the surveys made the 52 deposits contain a little less than 6,000,000,000 tons of the highest grade ore. In addition, loose high-grade ore was located to an amount as large as that found in the outcrops, the total high-grade ore located thus, amounting to 12,000,000,000 tons.

As Brazil, for various reasons, will be unable to work these vast deposits, they have recently been visited by representatives of American and British syndicates with a view to making contracts for ore shipments, in the immediate future, from Rio de Janeiro or from Victoria, about 300 miles north of Rio de Janeiro. The only result of these visits, as far as known, is the completion of a contract between a part of one of the British syndicates and the Victoria and Diamantina Railway Company for ore shipments *via* Victoria.

A conservation convention, which is to have the support of President Taft, in all probability, will be held in Indianapolis the latter part of September, for the benefit of the middle west. The movement for the convention has behind it Governor Marshall, of Indiana, and Henry Reisenberg, of that state, who plan to invite all the governors of the middle western states to participate. Mr. Reisenberg has been in Washington this week and he has discussed the project with the President.

The President has expressed a purpose to attend the proposed convention if it is held some time the latter part

of September, and deliver an address. Governor Marshall proposes that conservation shall be made part of the curriculum in the public schools of the western states. Mr. Reisenberg will return to Indiana at once, and letters soliciting the co-operation of middle western states will be sent out.

It is understood that the Union Pacific has completed plans for the establishment of large rolling mills and steel works in Greeley, Col., where steel rails for the western lines of the Harriman system will be made, as well as other products for cars and engines.

The plans, it is stated, are now in the New York offices awaiting the return of Mr. Harriman from Europe. Should they be adopted and the project carried out, it will mean employment for 2,000 to 3,000 men. It is believed that some of the buildings will be erected this year.

Since Mr. Harriman acquired the control of the Union Pacific, the Southern Pacific and the Oregon Short Line, he has felt the necessity of having steel works at some central point along the western portion of the system and, after making numerous trips back and forth from the coast, he has intimated that the most logical point would be in Colorado. He has said that to the south of Greeley less than 100 miles away there are mountains of iron and that in the western portion of the state and easy of access, there are inexhaustible quantities of coal, besides the great fields of Wyoming, owned and operated by the company. With these conditions existing, he has said that steel rails and the iron for cars and bridge work can be manufactured in Colorado at fully 25 per cent. less than is now paid for the same class of material at the mills of Pennsylvania, and 10 per cent. less than is now paid at the rolling mills of South Chicago.

Announcement is made by J. C. Edwards, of Spokane, that work on a 200-ton smelter at Hunters, Wash., 40 miles north of here will be begun this year. The project is being financed by Chicago people, interested in Stevens County properties. The smelter site is near the Columbia River where natural fluxes have been found in large quantities, convenient for handling, and in addition to the ore of the companies interested in the project, a custom business will be done for the district.

Mr. Edwards is expected to return from Chicago in three weeks, when the final arrangements will be completed and work started on the plant.

Palo Amarillo Rubber. Probable Yield of a Mexican Tree on Mountain Slopes.—In a report on Mexican rubber in *Daily Consular and Trade Reports* for January 26, 1909, references were made to the productivity of the palo amarillo tree, which are not sustained in the following report, transmitted by Vice-Consul-General C. Piquette Mitchel, of the City of Mexico, but prepared by Dr. Peter Glasson-Seffer, an agricultural and rubber report:

The palo amarillo tree, Euphorbia fulva, was discovered a few years ago on the slopes of the Sierra Madre, and upon investigation it was found to be a botanically unknown species. It is known in Mexico under a variety of common names, such as palo amarillo, palo colorado, papelillo, and cucuracho, the first-mentioned name being generally used. It occurs in the dry, semitropic zone on the slopes of Sierra Madre, at an elevation of 900 to 4,800 feet, generally being found above the oak zone and frequently reaching as high as to the pine zone of the mountains. It extends southward from Durango to the southern part of Oaxaca, along the Pacific coast, growing on rather poor, rocky or sandy volcanic soil, and it often forms a part of the xerophytic plant formations that have established themselves on the dry mountainside.

The tree grows to a height of between 20 and 34 feet, with a trunk diameter of from 7 to 12 inches.

In the inner bark of the stem and its branches occur numerous latex-bearing vessels containing a semiliquid fluid of milky whiteness, which solidifies upon contact with air. Chemical examination of this latex shows that it contains from 7.3 to 15.7 per cent. of rubber, and from 19 per cent. upwards of resin. I have personally analyzed seventeen latex samples from different parts of the tree and from trees growing in different soils. The latex from the lower parts of the trunk contains the higher percentages of rubber, as is the case with all rubber-producing trees. The branches carry a latex containing mainly resins, the rubber being about 3 to 6 per cent., and occurring in a form which makes it very difficult to be separated from impurities. The coagulation of the latex is not easy, although it can be accomplished. The resulting rubber is of inferior quality and would be commercially classed with guayule rubber, which has commanded a price of about 30 cents, where the price of first-class wild para rubber was 90 cents per pound during the last year when rubber prices have been low. It may be noted that rubber made according to modern methods from the ordinary Mexican rubber tree—*Castilla elastica*—has reached the highest standard of para rubber and has brought the same price. The tensile strength of palo amarillo rubber is 4 in scale where hard para rubber is taken as the standard of 12 points. The product of the palo amarillo tree being new, the test of time, which, after all, is the most important one, has not yet been applied, but taking into consideration the low tensile strength, the large percentage of resins, and the rapid deterioration of the latex through enzymes, it is not very likely that palo amarillo rubber will show a better result than the rubber obtained from the guayule shrub. The rubber is easy to vulcanize by the ordinary methods.

The exploitation of the latex of palo amarillo is connected with considerable difficulties.

It is claimed that the palo amarillo tree is very easily propagated. This is true, in so far as it refers to the actual reproduction of the individual. A young branch cut from a growing tree and planted in the ground will grow. Commercially this does not mean much, as a palo amarillo tree's exploitable age must be at least 10 to 11 years. A tree of this age does not give a very large amount of latex. The ordinary Mexican rubber tree, *Castilla elastica*, can be exploited when 8 years old, and it then gives a larger yield of latex per annum than a 10-year-old palo amarillo tree. Considering that the latex of the former contains from 25 to 47 per cent. of pure rubber, against about 8 per cent. in the palo amarillo latex, it is difficult to see the advantages of the latter under cultivation.

Taking even the most sanguine estimates in regard to the yield of palo amarillo, say as much as one kilo (2.2 pounds)

per day for two days, or a total latex yield of 4.4 pounds, the 8 per cent. rubber content would give a total of 5.03 ounces per tree. As a matter of fact, the yield is much less, and the average to be counted upon does not exceed one ounce of rubber per tree per year.

While it is certain that palo amarillo can be commercially exploited, the entire supply of the tree in the Republic of Mexico does not warrant the exaggerated estimates and plans recently published by certain promoters. The tree is spread over large areas, which can not be acquired by one corporation.

Directors of the Tennessee Copper Co. have decided upon the construction of another acid plant which will more than double the sulphuric acid producing facilities of the company. The present plant has a capacity of 300,000 tons of acid annually. Profiting by mistakes in the construction of the first acid plant, the company expects to be able to construct the new works at a cost of $800,000 against $1,000,000 for the original plant.

Lewisohn interests state that the amount actually received from the backers of the proposed fertilizer combine which J. P. Morgan & Co. were to finance and in which the Tennessee Copper Co.'s acid output was to play an important part, was $375,000 cash. Although the Morgan plans for the Independent Fertilizer Co. fell through, some of the manufacturers whose plants were to go into the merger, are working along quietly with the object of effecting a combine into which the Tennessee Co.'s acid business may enter.

This year no attempts have been made to increase the company's copper output, which is being maintained at the rate of 15,000,000 pounds. The acid plant is operating about 50 per cent. of its capacity and the company is marketing its own product.

No action has been taken by the directors for the resumption of dividends which have been suspended for nine months.

The Belgian Government recently instructed M. Decamps, one of the leading engineers of the state railways, to study the question of the use of silicon steel rails in England, concerning which Consul H. Abert Johnson writes from Liege:

The results of his investigations have been studied with considerable interest by railway specialists here, as it appears that rails made of silicon steel have been used by the Southeastern and Chatham Railway since 1904, and subsequently, by several other lines, as well as by the Metropolitan, of London, and various street railway lines.

The investigation on the part of M. Decamps is, it is asserted, absolutely conclusive, as it is shown that rails of this class will far outlast those heretofore in use. The process of manufacture results in increasing the compactness of the metal, while at the same time rendering it more ductile, augmenting in a remarkable degree its capacity for resisting violent shocks. This latter characteristic, in regard to which experts have been somewhat skeptical, has been demonstrated by several years' experience, and is an element which especially enhances its superiority.

The modifications in the process of manufacture of this class of steel are as follows: Ferrosilicon, containing 75 per cent. of silicon, is put into the casting ladle; two special operations are performed after the rail has passed through the rolling mill; the flange is cooled by a jet of water; after this the rail is allowed to cool before placing it in the finishing machine for grooving. The process of cold-rolling produces a finer-grained metal, it is claimed. Experiments with silicon steel rails will be made on the inclined plane from Liege-Guillemins station to Ans, and on the line from Luxemburg, two sections of Belgian lines that are called upon to resist the heaviest strain.

It is asserted that the manufacture of silicon steel will tend to develop, to a certain extent, the qualities of Bessemer steel for which silicon ores are utilized, while in the making of Thomas steel, which at present tends to monopolize the furnaces of this region, phosphorous ores are required.

OFFICIAL REGULATIONS AND RULINGS.

(T. D. 1509). *Distilled Spirits.* Question of substitution or addition of caramel.—Test case decided in favor of the Government.—T. D. 1325 revoked.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
Washington, D. C., June 9, 1909.

To Collectors of Internal Revenue, Revenue Agents, and All Others Concerned:

By T. D. 1325 of February 26, 1908, this office gave notice that no further seizures of (double-stamped) spirits would be made on the ground of the addition of caramel, or for substitution, when the proof of substitution depended upon the presence of caramel, or upon the result of chemical analysis, until a test case then pending had been heard. All packages of spirits then under seizure for this cause were ordered released.

The test case has now been tried and decided in favor of the Government and against the claimant. And upon the advice of the honorable Attorney-General the suspension of action by internal-revenue officers directed by T. D. 1325 is hereby revoked, to take effect July 1, 1909, and all internal-revenue officers and others concerned will govern themselves accordingly.

ROBT. WILLIAMS, JR., *Acting Commissioner*

(T. D. 29828). *Importation of Viruses, Serums, Etc., Under Act of July 1, 1902.*

TREASURY DEPARTMENT, June 10, 1909.

To Collectors and Other Officers of the Customs:

The following excerpt from the act of Congress approved July 1, 1902, and regulations thereunder are published for the information and guidance of all concerned.

JAMES B. REYNOLDS, *Acting Secretary.*

An act to regulate the sale of viruses, serums, toxins, and analogous products in the District of Columbia, to regulate interstate traffic in said articles, and for other purposes.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, That from and after six months after the promulgation of the regulations authorized by section four of this act no person shall * * * bring for sale, barter, or exchange from * * * any foreign country into the United States,

* * * any virus, therapeutic serum, toxin, antitoxin, or analogous product applicable to the prevention and cure of diseases of man, unless such virus, serum, toxin, antitoxin, or product has been propagated and prepared at an establishment holding an unsuspended and unrevoked license, issued by the Secretary of the Treasury as hereinafter authorized, * * * nor unless each package of such virus, serum, toxin, antitoxin, or product is plainly marked with the proper name of the article contained therein, the name, address, license number of the manufacturer, and the date beyond which the contents can not be expected beyond reasonable doubt to yield their specific results. * * *

Approved July 1, 1902.

The Board of Food and Drug Inspection has issued the following judgment notices:

July 13.

69. Misbranding of rye flour (as to presence of wheat).

70. Misbranding of canned peas (underweight).

71. Misbranding of lemon extract (as to presence of lemon oil).

72. Misbranding of canned cherries (underweight).

73. Misbranding of vinegar (colored imitation fruit vinegar.

74. Misbranding of maple sirup (as to presence of cane sugar sirup).

75. Adulteration and misbranding of pepper (as to presence of nut shells, fruit pits, etc.).

76. Adulteration of oats (as to presence of barley).

77. Misbranding of canned tomatoes (underweight).

78. Misbranding of water (as to origin and source).

79. Misbranding of tomato catsup (as to presence of screenings and waste).

80. Misbranding of salad oil (as to origin).

81. Adulteration of milk (water).

June 30.

82. Misbranding of drug preparations (Mme. Yale's skin food, etc.).

FOOD INSPECTION DECISION 108.

Importation of Coffee.—The Department has recently investigated the sale and shipment, within the jurisdiction of the Food and Drugs Act of June 30, 1906, of decomposed, imperfect and damaged coffee. A public hearing on this subject was held by the Board of Food and Drug Inspection on December 15, 1908, at which an opportunity to be heard was given to the trade and to the public.

As a result of the investigation and the evidence adduced at the hearing, it is announced that the product ordinarily known as "Black Jack," consisting of rotten or decomposed berries, is regarded by the Department as injurious to health and the Food and Drugs Act forbids its shipment or sale within the jurisdiction of the said act. Coffee which is damaged by water during shipment, or which has acquired a permanently offensive odor because of its proximity to hides or other material of objectionable odor, is considered by the Department to come within the phrase "filthy, decomposed, or putrid," within the meaning of that phrase as used in the Food and Drugs Act, and its shipment or sale as hereinbefore stated, is therefore held to be forbidden. Immature berries, ordinarily known as "Quakers," are dead beans without pronounced smell or taste. They have not the characteristics of coffee, and, in the opinion of the Department, their shipment or sale as coffee within the jurisdiction of the Act is in violation thereof.

It is recognized that the ordinary coffees of commerce usually contain small quantities of these inhibited products, and no action will be taken in regard to the shipment or sale of the recognized graded coffees of commerce because of the small amount of these substances which may be present. In determining the present action of the Department on any particular lot as to whether it contains more than the ordinary small quantities of the inhibited products, coffee graded as No. 8, on the New York Coffee Exchange, will be taken as a standard.

Screenings consisting of inferior or broken berries, of stones, sticks, dirt, etc., should not be sold as coffee even in a ground condition. This product should be designated as "Coffee screenings."

F. L. Dunlap,
Geo. P. McCabe,
Board of Food and Drug Inspection.

Approved:
James Wilson,
Secretary of Agriculture.
Washington, D. C., *June 15, 1909.*

Chilean Nitrates.—Consul Alfred A. Winslow, of Valparaiso, submits the following report in regard to the condition of the nitrate business in Chile:

The nitrate business is badly disturbed over the dissolution of the nitrate combine that ended March 31, 1909. The price of nitrate has declined very materially, and several of the works have shut down. A strong effort is being made to agree again upon some working basis, so as to control the market and keep up the price. The Chilean Government is taking a hand in the matter, since it is deeply interested, as there is an export tax of 56 cents United States gold per Spanish quintal of 101.42 pounds.

On January 31, 1909, there were 145 separate nitrate works in Chile, and it is a very difficult matter to get all the interests together. There are several strong companies that own several plants each, and it is among these that the most opposition to combining is found.

The following table covers the average cost of nitrate per quintal in United States gold under the several conditions given during the month of May for the years 1905, 1906, 1907, and 1908.

Selling condition	1905	1906	1907.	1908.
On board steamer in Europe	$2.46	$2.38	$2.21	$2.12
On board steamer in Chile with freight paid	2.26	2.34	2.46	2.19
Alongside steamer in Chilean port	1.84	1.96	2.13	1.79

During May, 1909, the price of nitrate was quoted as low as $1.60 United States gold per quintal, to be delivered alongside steamer in Chilean ports.

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EDITORIALS.

INDUSTRIAL INCOMPATIBILITIES.

The physician and the pharmacist are vitally concerned with the subject of incompatibility as applied to substances in the materia medica, and they must be on guard against therapeutical, pharmaceutical and chemical incompatibilities if their prescribing and dispensing are to be productive of good. A thorough knowledge of the properties of their medicines and the proper application of chemical and physical principles have led them to the refined pharmaceutical products of to-day—products that contrast strongly with the crude medicaments of a century ago.

Is there not something of the same sort in the industrial world? One does not have to go very far back into the history of manufacturing processes to discover marked "incompatibilities" among industries. The introduction of the Le Blanc soda process resulted in the formation of large quantities of hydrogen chloride which simply escaped through the chimneys and caused great damage to the surrounding country; the ammonia liquor and tar from gas works found their way into drains and rivers; refuse from slaughterhouses constituted no mean nuisance; and even the offal and waste from the houses of a mediaeval city became a source of infection. Thus air, water and the very earth itself were rendered unfit for many industries and offensive to the senses of man.

But with the pressure of stern necessity for improved conditions laid upon the manufacturer, and with the growth of new industries, there were developed ways for utilizing the hydrochloric acid, ammonia, tar, packing-house refuse, household garbage and even sewage. The chemical fertilizer, made from factory wastes that had been a menace to agriculture, proved to be the salvation of exhausted farm land; and purified ammonia and coal-tar colors advanced the art of the bleacher and dyer who had complained about the pollution of his water supplies by gas works refuse. Industrial incompatibility gave way before technical progress.

Similar results can be expected in the cases of the industrial incompatibilities that remain. The elimination of the coal smoke nuisance, the conversion of smelter gases into valuable products, the proper treatment of mine waters, the cure of the dust evil at manufacturing plants of various kinds, are problems by no means incapable of solution in the near future. As heretofore industrial incompatibility will be replaced by industrial interdependence, but meanwhile the principle of "live and let live" must be exercised or the law of nuisance invoked.

W. C. Ebaugh.

COMMITTEES.

The man who remarked very thoughtfully that a committee was a body which took a week to do something which could be done by a good man in an hour, was nearly correct. And yet the necessity for committee work has increased and is sure to increase in the future with a civilization which is

developing along coöperative lines. Committee work is in its nature coöperative even when directed or dominated by an individual.

For the chemist and the engineer the greatest need for committee work has been for the purpose of standardizing and developing methods of testing, sampling and analysis. Various chemical and engineering societies have appointed such committees from time to time as occasion seemed to require. Some of these committees reported in due time; others, either from the complexity of the problem laid before them or because of lack of enthusiasm for the work, more than lived up to the pessimistic definition given above and never reported at all. On the whole, the most systematic work of this sort which has heretofore been performed, must be credited to the Association of Official Agricultural Chemists. Beyond question this organization, through its referees, has developed and systematized more methods (and these in a difficult field of analysis) than any other single chemical society in this country or in the world. In a different field the American Society for Testing Materials and the International Society are doing excellent work. The American Chemical Society has done much in a few limited fields to further the work. The Geological Survey and the Bureau of Standards have contributed. So have the American Foundrymen's Association and the American Brass Founders' Association. The National Fertilizer Association has had a committee at work upon methods of fertilizer analysis, the American Leather Chemists' Association has worked on methods of interest to its members, the United States Steel Corporation has a committee on steel and ore analysis. The latest development is the coöperative committee, consisting of committees appointed by two or more societies, working together on the same subject.

The necessity for committee work being granted and the desirability of perfected and codified methods of testing, sampling and analysis being manifest, nevertheless is there not a certain amount of danger here in having so many committees working on similar subjects? To be sure, up to the present time there has not been much duplication of work or overlapping of territory but there has been some. The fact that so many organizations of diverse character feel at liberty to appoint committees on the subject carries with it the certainty that duplication or conflict will ensue as time goes on. There is also the danger of having too many chemical cooks in the kitchen. It would be unfortunate if any perfunctory or ill-considered work were to be done in the building up of standard methods. There have been indications during recent months that certain referees and committees were working more in the direction of issuing reports than of performing necessary and useful work, and of adding to the present difficulties by the addition of new methods no better than the old, rather than by the elimination of all but the best. The official recognition of a method no better than the current one or only "just as good" is hardly justifiable. It adds to the confusion. Improvement, simplification, and elimination are the things to be desired. Also the centralization of the work in the hands of a few recognized and representative organizations.

ORIGINAL PAPERS

THE ASH OF COAL AND ITS RELATION TO ACTUAL OR UNIT COAL VALUES.

By S. W. Parr and W. F. Wheeler.

Received July 1, 1909

In the report of the committee of the American Chemical Society on coal analysis,[1] occurs this question: "Are carbonates likely to be present in the ash in such amounts that heating over a blast lamp would lessen the weight appreciably?"

In studying the properties of the organic constituents or actual coal substance as distinct from the inorganic material, it was found necessary to scrutinize more carefully the methods for obtaining these inorganic values. In directing our attention to the ash itself, considerable evidence accumulated to the effect that carbonate of lime was a constituent part of the coal. In taking up this matter, therefore, with a view to determining the extent and quantity of this material, fifty samples of Illinois coal were selected covering all the important districts of the state. An analysis was made of the carbonate content of each and a further analysis was made of the mineral constituents of the ash. Test was also made as to the presence of chlorine and this element was determined in addition. The methods employed were those already well known and familiar to all chemists. In the case of chlorine, a five-gram sample of coal, ground to pass a 100-mesh sieve, was digested with water and filtered and this filtrate taken for the determination of

[1] *Jour. Am. Chem. Soc.*, **20**, 284 (1898).

chlorine by the usual volumetric process by means of a standard solution of silver nitrate. It was only necessary to guard against acidity and in some instances the iron was present to an extent requiring its removal. In the case of the carbonates, a determination was made of the amount of carbon dioxide present by liberating the same with acid and determining the amount volumetrically. For this purpose the apparatus shown herewith (Fig. 1) was used.

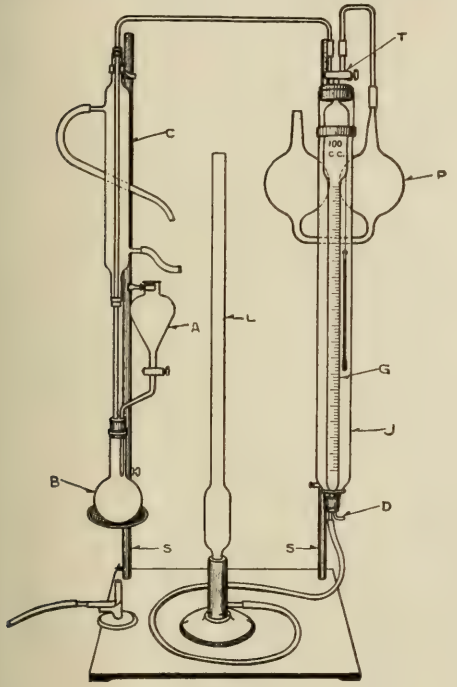


Fig. 1.

This is a modification of the apparatus already described in the determination of total carbon in coal, soils, etc.[1] By this apparatus the carbon dioxide liberated is absorbed by the large pipette, P (Fig. 1) and the residual gas returned to the burette for reading. The contraction in volume thus indicates the amount of CO_2 present, and this volume is transferred to gravimetric terms by reference to the table recently published in this Journal[2] The entire list of values for the fifty samples is published in *Bulletin*, —— of the Engineering Experiment Station of the University of Illinois under the title, "Unit Coal and the Composition of Ash."[1]

[1] *Jour. Am. Chem. Soc.*, **26**, 294 (1904).

[2] *Ibid.*, **31**, 237 (1909).

Only fifteen of the samples are selected for reproduction here. These consist of numbers giving the higher percentages of carbon dioxide and of chlorine. It should be said, however, that while the remaining samples fall below one per cent. of carbon dioxide, the average for the other samples would be considerably over 0.5 per cent. If we consider all the carbon dioxide present as being combined in the form of calcium carbonate it is readily seen that in not a few instances, coal, at least from the Illinois field, may have an amount of this constituent ranging from three to five per cent.

TABLE I—ANALYSIS OF COAL ASH.

Description.				Dry coal basis.			
Tab. No.	Lab. No.	Location.	Seam No.	Ash by usual method. Per cent.	CO_2. Per cent.	Cl. Per cent.	CaO. Per cent. in fused ash.
1*	734	Coal City, Grundy Co.	2	5.82	0.88	None	34.0
2	1411	Hollis, Peoria Co.	2	10.90	0.98	0.27	18.6
3	896	Spillerton, Williamson Co.	5	10.68	0.70	0.31	3.9
4*	1085	Eldorado, Saline Co.	5	11.49	1.22	0.04	25.3
5	1116	Ledford, Saline Co.	5	9.89	1.51	0.05	26.5
6	720	Lincoln, Sangamon Co.	5	13.81	0.54	0.32	30.8
7*	1403	Bartonville, Peoria Co.	5	15.46	2.48	None	54.5
8	1404	Canton, Fulton Co.	5	12.52	1.30	None	22.4
9	1407	Edwards Sta., Peoria Co.	5	16.25	2.15	0.03	31.1
10	1410	Maxwell, Peoria Co.	5	14.78	1.57	None	31.3
11	1413	Pekin, Tazewell Co.	5	...	1.36	None	31.6
12	557	Westville, Vermillion Co.	5	9.15	1.08	0.15	5.6
13*	1178	Trenton, Clinton Co.	6	15.56	2.48	0.10	31.7
14	420	Zeigler, Franklin Co.	7	7.53	0.21	0.55	6.3
15	422	DuQuoin, Perry Co.	7	...	0.28	0.47	6.7
16	1120	Gelatia, Saline Co.	7	...	1.20	0.07	11.6

In the further prosecution of our studies, it was desired that an accentuation of these carbonate conditions be obtained which was done in the following manner: Four samples were selected from among the lot of fifty and these are indicated by stars in Table I. These samples in buckwheat size were subjected to the floating process wherein a solution of calcium chloride, 1.35 specific gravity, was used. By this means those portions of coal low in ash and high in organic constituents would rise to the surface. Each sample of coal was thus made to yield two subdivisions, one very low and the other very high in ash. Table II will illustrate this fact. By subjecting these artifically prepared samples to the same process of analysis the chlorine and carbon dioxide values are at once shown. It

[1] *Bull.* —, *E. E. Sta.*, S. W. Parr and W. F. Wheeler.

is evident from an examination of the column for chlorine that this material was not completely washed out after application of the floating process, since the percentage amount is practically the same in both divisions and altogether higher in amount than the normal quantity in the coal, as is evident by reference to the values in Table I.

TABLE II.—ASH CONSTITUENTS OF FLOAT AND SINK COAL.

			Dry coal basis.			
Tab. No.	Lab. No.	Description.	Ash by usual method. Per cent.	CO_2 Per cent.	Cl. Per cent.	CaO MgO in fused ash, per cent.
1	734	Float, Grundy Co., Ill.........	4.57	0.10	1.00	0.85
2	734	Sink, Grundy Co., Ill..........	21.99	3.68	1.15	6.50
3	1095	Float, Saline Co., Ill...........	6.42	0.13	0.17	0.40
4	1095	Sink, Saline Co., Ill...........	19.94	2.38	0.31	3.88
5	1178	Float, Clinton Co., Ill.........	8.54	0.21	1.41	0.88
6	1178	Sink, Clinton Co., Ill..........	31.90	5.27	1.20	8.36
7	1403	Float, Peoria Co., Ill..........	10.37	0.37	1.07	1.29
8	1403	Sink, Peoria Co., Ill...........	34.24	7.35	1.17	10.20

It is evident that in these samples we have an excellent opportunity for testing the effect of a high content of calcium carbonate upon the ash as determined by a use of higher or lower temperature. Determinations were therefore made in the usual manner and also by carrying the heat by means of a blast lamp to the fusion point and repeated until a constant weight was obtained. The results are given in Table III.

TABLE III—VARIATIONS IN ASH VALUES WHERE CALCIUM CARBONATE IS A CONSTITUENT OF THE COAL.

Tab. No.	Lab. No.	Description.	*a.* Ash as determined by usual method. Per cent.	*b.* Ash as determined by blasting to constant weight and fusion. Per cent.	*c.* Difference in per cent of dry coal. Per cent.	*d.* Ash corrected for CO_2 and Cl. Per cent.
1	734	Float, Grundy Co., Ill	4.57	3.54	1.03	4.64
2	734	Sink, Grundy Co., Ill......	21.99	16.85	5.14	21.68
3	1095	Float, Saline Co., Ill.......	6.42	5.96	0.46	6.26
4	1095	Sink, Saline Co., Ill.......	19.94	18.59	1.35	21.28
5	1178	Float, Clinton Co., Ill.....	8.54	7.23	1.31	8.85
6	1178	Sink, Clinton Co., Ill......	31.90	26.88	5.02	33.35
7	1403	Float, Peoria Co., Ill......	10.37	9.08	1.29	10.52
8	1403	Sink, Peoria Co., Ill.......	34.24	22.93	11.31	31.45

In this table there is presented the differences which result from these two methods. It becomes, therefore, an answer to the question raised by the committee as to the effect of heating over a blast lamp and the consequent lessening of weight. It is true these samples are exaggerated cases, but it is none the less true that for the purposes for which these samples were being used, namely, a study of the actual coal constituents, it was necessary that a correct determination of the ash be secured. The first evidence of difficulty occurred in all cases where the high ash content was present, or in the "sink" sample, by reason of the uncertainty involved in securing concordant weights in the duplicate determinations. Evidently the application of a little more or a little less heat results in the decomposition of more or less of the calcium carbonate. However, under column (*a*) the ash as determined by the usual method was obtained with as good an agreement as possible, although a variation of two per cent. in results was frequently met with by this method. In column (*b*) the heat was carried to the point of fusion and the application of the blast was repeated until a constant weight was secured. It is certainly a striking illustration of the possible difference in results when we examine, for example, samples No. 8 of Table I and see a variation in values from 34.24 per cent. to 22.93 per cent., or a difference of over 11 per cent. in the value for ash as obtained by the two processes. Similarly unallowable, though not such extreme differences are found in the other high carbonate samples of the table. It must be obvious from such values that some other method must be resorted to for securing the correct ash values if we are to arrive at any correct conclusions in our study of the actual or organic part of the coal. The method followed in these samples of Table III was to carry the high temperature in a platinum crucible to the fusion point or to the point of constant weight. By then adding to the weight of ash thus obtained the percentage of carbon dioxide as obtained by the process already outlined and also the weight of chlorine, a percentage of ash was secured quite different from any of the values indicated in Table II or III. These values are shown in column (*d*) and consist of the values in column (*b*) plus the carbon dioxide and the chlorine indicated in Table II.

The results of the facts thus far set forth are somewhat disconcerting to some of our established methods, notably the values obtained by ultimate analysis. In the case of a coal with one or two per cent. of carbon dioxide in the form of calcium carbonate the total carbon as obtained by means of the combustion furnace would be high and the error thus involved would extend throughout all the determinations, such as the amount of oxygen, available hydrogen and the calculation of the heat values by DuLong's formula. Moreover, the error involved in the ash determination

itself would affect the calculations to the "ash and water-free" basis or other methods for arriving at so-called "pure coal" values.

ACTUAL OR UNIT COAL.

As has already been indicated the initial necessity for determining the correct value for ash and inorganic constituents resulted from our studies upon the character and constancy of the composition of the organic or actual coal constituents. If, for example, it is conceded that in a given sample of coal which had been subjected to the floating out process the organic or actual coal of the "float" part is substantially the same and would have the same heat value as the organic constituents of "sink" coal, then when reduced to this "pure coal" basis the heat values should closely correspond. If there is wide disagreement, then we must conclude that our values for ash are in error, and that a correct ash or inorganic factor would bring these values when calculated to the "pure coal" basis in substantial agreement. As illustrating this point, Table IV is presented which takes the heat values as indicated on the "dry coal" basis and calculates them to the "ash free" condition, taking the ash value as obtained by blasting to a constant weight as already indicated in Table III. The heat values thus obtained are so widely apart as to indicate at once a wide error in our ash values.

TABLE IV.—"UNIT COAL" IN SAMPLES WITH HIGH CALCIUM CARBONATE.

Tab. No.	Lab. No.	Description.	In per cent. of dry coal. Ash as determined by high fusion to constant weight.	CO_2.	Cl.	B. T. U.	"Pure coal." $\frac{\text{B. T. U.}}{1.00 - \text{ash}}$	Diff.
1	734	Float........	3.54	0.10	1.00	13475	13969	
2	734	Sink..........	16.85	3.68	1.15	10733	12908	1061
3	1095	Float...........	5.96	0.13	0.17	13663	14528	
4	1095	Sink...........	18.59	2.38	0.31	11122	13662	866
5	1178	Float...........	7.23	0:21	1.41	12634	13618	
6	1178	Sink...........	26.88	5.27	1.20	8856	12111	1507
7	1403	Float...........	9.08	0.37	1.07	12796	14073	
8	1403	Sink...........	22.93	7.35	1.17	9216	11941	2132

It is to be noted that these differences range from over 800 to over 2000 B. T. U., which is a difference of from 6 to 15 per cent. Aside from its bearing upon the method of ash determination, the subject of the heat values to be attributed to the values of actual or unit coal is one of great importance, not only in the scientific study of this subject, but in its practical bearing in connection with coal contracts and coal inspection work. That the importance of this matter has long been recognized may be seen from reference to the work of Lord and Haas,[1] who were the first to call attention to the matter and gave extended analytical data to prove the constancy of heat values over large areas when referred to the actual or unit coal. W. A. Noyes[2] called attention to similar conclusions concerning the Indiana field. The practical value of this fact as substantiated, especially in the matter of coal inspection, has been urged by Mr. Bement.[3] A true appreciation of the practical importance of the subject seems, therefore, to have been revived by him. A point at issue, however, has been raised as to the method of arriving at these so-called "pure coal" values. A graphical method has been suggested by Taylor and Brinsmaid.[4] Although indirect and resting entirely on empirical data for a given region, it is no doubt of much practical value. It has been the effort of the authors of this paper, in so far as it is possible, to arrive by direct analysis at the inorganic constituents and, as contributing to this end, the determination of the carbon dioxide and the chlorine content are in evidence. In combating the method ordinarily employed for arriving at the heat values on the "pure coal" basis, it was argued by Parr[5] that not only was the sulphur a disturbing element in the case, but certain volatile elements were present which escaped determination as part of the ash and were therefore included in the actual coal, thus introducing a variable which prevented the obtaining of accurate values for that substance. For example, if the shaley constituent of the ash is hydrated, or if other volatile material is chemically combined with the mineral or ash substance in such a manner that it would be driven off only at red heat, then an error in calculation would result equivalent to the amount of such hydration. Analytical data in support of this contention has been furnished by Mr. Wheeler,[6] and it is the purpose of this part of the discussion to carry forward the evidence along this line. As the most suitable medium for arriving at the point in question the samples already referred to as being separated into "float" and "sink" divisions or subdivisions of the same coal into samples of low and high ash

[1] *Trans. Am. Inst. Mining Engs.*, **27**, 259 (1898).
[2] *Jour. Am. Chem. Soc.*, **20**, 285 (1898).
[3] *Ibid.*, **26**, 636 (1906).
[4] THIS JOURNAL, **1**, 65 (1909).
[5] *Jour. Western Soc. of Eng.*, **2**, 1762 (1906).
[6] *Trans. Am. Inst. Mining Engs.*, **38**, 621 (1908).

content, a number of coals have been so treated and results are given in Table V.

Now, upon the hypothesis that the actual or unit coal in these two divisions of the same sample should have the same heat value, we have listed under columns (*a*), (*b*), (*c*) and (*d*) the values obtained by different methods of calculation, on the theory that those which most closely agree in the two divisions of the same sample have arrived the most closely in the percentage values to be attributed to the ash or inorganic substance.

If we credit, for example, to the actual coal everything excepting the ash as weighed, and the moisture, we shall have unit values as shown under column (*a*). This is the "pure coal" of Bement.

If we take out the heat due to sulphur and correct the remaining value for ash as determined plus the moisture plus all of the sulphur, we shall have the value as derived for column (*b*), which would be the results obtained by means of the method suggested by Lord and Haas.

Under column (*c*) we have the method suggested by Dr. Noyes, the results of which are obtained by calculating the indicated values over to the material as free from ash and moisture and correcting the ash further for one-half of the sulphur.

In column (*d*) there is introduced as a natural component of the ash an amount of hydration equal to 8 per cent. of the ash. There is a further correction for sulphur which in the original coal is considered as in the form of iron pyrites. A tabulation of these several methods of calculation, therefore, would be as follows:

(*a*) According to Bement,

$$\frac{\text{B. T. U. as indicated}}{1.00\ (\text{Moisture} + \text{ash as weighed})}$$

(*b*) According to Lord and Haas,

$$\frac{\text{B. T. U.} - 4050\ \text{S.}}{1.00 - (\text{Moisture} + \text{ash as weighed} + \text{sulphur})}$$

(*c*) According to Noyes,

$$\frac{\text{B. T. U. as indicated}}{1.00 - (\text{Moisture} + \text{ash as weighed} + 1/2\ \text{sulphur})}$$

(*d*) According to Parr and Wheeler,

$$\frac{\text{B. T. U.} - 5000\,\text{S}}{1.00 - (\text{Moisture} + \text{ash} + 5/8\ \text{S} + 0.08(\text{ash} - 10/8\ \text{S})}$$

The method of deriving a formula embodying the conditions prescribed under (*d*) would be as follows:

First, with reference to the subtraction of the heat due to the sulphur. It should be borne in mind that the purpose of this study is, first to arrive at the actual weight of unit coal as represented by the expression 1.00—(all non-coal constituents); and second, to derive the actual heat per unit weight to be credited to this material, by dividing the indicated heat for this substance by the weight which produces it. Hence, for this particular purpose the sulphur must be eliminated, both as to its heat value and as to its weight in the material whose value is sought for. This procedure may not suit the purpose of the engineer who has in mind only the available heat without reference to its source, but that is a matter quite apart from the facts which it is the purpose of this discussion to establish.

Second, the expression 5000 S has been used as indicating the heat due to the combustion of the sulphur for the reason that the value 4050 S as used in formula (*b*) represents the heat of combustion for pure sulphur, while the heat of combustion of sulphur in the form of iron pyrites, FeS_2, combines also the heat of formation of iron oxide, Fe_2O_3. It is the resultant value, therefore, of the several reactions involved that is desired.

According to direct tests by Somermeier,[1] in the combustion of coal with known weight of iron pyrites, the indicated heat per gram of sulphur so combined is 4957 calories. In calculating heat values the correction introduced for the combinations resulting from calorimeter reactions as compared with open-air combustion is 2042 calories per gram of pyrite sulphur, hence 4957 — 2042 or 2915 calories (5247 B. T. U.) represent the heat due to the burning of one gram of sulphur in pyritic form instead of 2250 calories (4050 B. T. U.), the amount which would be credited to sulphur in the free condition. A strict application of these values, therefore, would call for a correction of 5247 S as representing the heat to be subtracted for the sulphur. This, however, would imply that all of the sulphur is in the pyritic form. Since a certain portion of the sulphur is always present in the organic or other form of less heat-producing capacity, it is deemed more nearly correct to use an even factor of 5000 as representing the heat to be credited to unit amounts of the total sulphur present.

The factors for the divisor in the formula under (*d*) are derived as follows:

[1] *Jour. Am. Chem. Soc.*, **26**, 566.

The atomic ratio of iron to sulphur in iron pyrites (FeS_2) is 56:64.

That is, 7/8 of the total sulphur is the equivalent of the iron present as Fe.

The atomic ratio of the oxygen of the ash combined as Fe_2O_3 to the total sulphur which it replaces is 48:128.

That is, 3/8 of the total sulphur is the equivalent of the oxygen present in the ash combined as Fe_2O_3, hence the ash as weighed may be corrected for the iron pyrites FeS_2 burned to Fe_2O_3 by subtracting from the ash 10/8 of the weight of the sulphur as determined. This remainder, therefore, is considered as the shaley and carbonate constituent upon which the 8 per cent. of water of hydration, carbon dioxide, etc., is calculated. The expression for the total non-coal substance then becomes

Non-coal = moisture + ash as weighed + 5/8 S + 0.08 (ash — 10/8 S).

This expression can be simplified as follows:

Clearing of fractions and combining we have

Non-coal = moisture + 1.08 ash + 21/40 S.

In this expression the factor 21/40 S can not be further simplified by making it 1/2 S for the reason that our correction for sulphur is already too small by that part of the organic sulphur not covered by the addition to the ash value of 3/8 of the total sulphur indicated in the original formula. On the contrary, we will be approaching nearer the truth by increasing slightly the sulphur correction which may be done with convenience in calculating by making this factor read 22/40 S or 1/2 S + 1/20 S.

Hence the simplication of the entire formula under (*d*) would be

B. T. U. or unit coal =

$$\frac{\text{Indicated B. T. U.} - 5000\ \text{S.}}{1.00 - (\text{Moisture} + 1.08\ \text{ash} + 1/2\ \text{S} + 1/20\ \text{S})}.$$

Since the analytical values given in the table are based upon the coal as oven-dry, of course the moisture factors in the above formulae drop out and would not enter into the calculations. In the table, for example, sample No. 1 has an indicated B. T. U. for the dry coal of 12356. The calculations, therefore, for each column are:

$$(a) = \frac{12356}{1.00 - 0.1166} = \ldots\ldots 13{,}987$$

$$(b) = \frac{12356 - 4050\ (0.0599)}{1.00 - (0.1166 + 0.0599)} = \ldots 14{,}709$$

$$(c) = \frac{12356}{1.00 - (0.1166 + 0.0299)} = \ldots 14{,}477$$

$$(d) = \frac{12356 - 5000\ (0.0599)}{1.00 - (1.08\ (0.1166) + 0.02995 + 0.00299)} = 14{,}331$$

In Table V, which follows, the actual or unit coal values for the two subdivisions of each sample are in such close agreement under the last formula—the values for which are given in column (*d*)—that it would seem fair to conclude that a correct factor for the inorganic constituents is represented by the factors in that formula. This is true at least for the samples chosen.

TABLE V—COMPARATIVE VALUES OF "ACTUAL COAL"

Table No.	Lab. No.	Description of sample.	Oven-dry coal. Ash.	Sulphur.	B.T.U.	Heat values of "actual coal" as calculated by different methods. (*a*) Non-coal as ash only (uncorrected) Ref to indicated B. T. U.	Diff.	(*b*) Non-coal as ash (uncorrected) + sulphur ref. to B. T. U. —4050 S.	Diff.	(*c*) Non-coal as ash + 1/2 sulphur ref. to B. T. U. as indicated.	Diff.	(*d*) Non-coal as 1.08 ash + 22/40 S. Ref. to B.T.U.—5000 S.	Diff.
1	6130	Sangamon County, Ill. Lump coal:											
		(*a*) Untreated	11.66	5.99	12356	13987		14709		14477		14331	
	6131	(*b*) Floated, sp. gr. less than 1.35	6.12	3.20	13300	14164	+177	14523	—186	14412	—65	14340	+9
2	6129	LaSalle County, Ill Washed screenings:											
		(*a*) Untreated	10.05	3.43	12885	14316		14616		14602		14566	
		(*b*) Floated, sp. gr. less than 1.35	3.94	2.33	13922	14487	+171	14754	+138	14680	+78	14615	+49
3	6132	Virgo County, Indiana. Nut:											
		(*a*) Untreated	16.84	7.62	11790	14170		15230		14858		14698	
	6133	(*b*) Floated, sp. gr. less than 1.35	4.27	3.08	13870	14478	+308	14836	—394	14725	—133	14638	—60
4	6135	Sullivan County, Indiana. Lump:											
		(*a*) Untreated	6.11	3.37	13664	14551		14944		14819		14741	
	6134	(*b*) Floated, sp. gr less than 1.35	2.53	1.29	14259	14624	+73	14771	—173	14820	+1	14700	—41
5	471	Franklin County, Ill. Face sample:											
		(*a*) Sp. gr. greater than 1.35	18.00	0.57	11639	14194		14236		14244		14467	
	463	(*b*) Sp. gr less than 1.35	4.64	0.54	13765	14435	+241	14492	+229	14476	+232	14513	+46
6	472	Perry County, Ill. Face sample:											
		(*a*) Sp. gr greater than 1.35	22.17	1.15	10922	14033		14183		14136		14405	
	465	(*b*) Sp. gr less than 1.35	4.22	0.86	13763	14369	+336	14464	+281	14434	+298	14446	+41
7	473	Williamson County, Ill. Face sample:											
		(*a*) Sp. gr. greater than 1.35	17.75	1.15	11766	14306		14451		14405		14599	
	467	(*b*) Sp. gr. less than 1.35	4.08	0.99	13942	14535	+229	14644	+193	14617	+212	14615	+16

An extended compilation[1] has been made covering results from this laboratory and from the United States Geological Survey and also from the Ohio State Survey. The values derived for a given locality or geological seam are in such good agreement as to still further substantiate this method for arriving at the true ash values. There is thus afforded, moreover, a method for arriving directly at the amount, and consequently the heat value, of that portion of the coal substance which we have designated as actual or unit coal.

University of Illinois,
Urbana, Illinois.

[1] *Bull* **37**, *University of Illinois, Eng Exp Sta*

THE TECHNICAL APPLICATION OF TITANIUM.

By Isador Ladoff

Received July 17 1909.

Titanium so far has found only one application; namely, coloring porcelain, artificial teeth, leather and textiles.

Almost ten years ago an English firm made the first attempt to utilize titanium compounds for coloring purposes. The process used by that firm was as follows: Twelve pounds of caustic soda were melted in an iron kettle of three and one-half gallons, over a coke fire. The molten mass was left for a time at dark red heat and three pounds of ground rutile containing 80–90 per cent. titanic acid (TiO_2) were added in small portions. The mass was mixed with an iron rod frequently and kept at a high temperature during an hour. The fused conglomerate was poured on an iron slab and allowed to cool. The brittle mass was then pulverized and digested with cold water during 48 hours and stirred at intervals. The insoluble portion was freed by frequent change of water and filtration. The superfluous caustic was removed, while the hydrated oxide of titanium remained. The washed and filtered oxide was digested in 2 3/4 gallons of cold 30 per cent. hydrochloric acid during one to two days, and frequently stirred. During this process the temperature was not allowed to exceed 38° C. The hydrochloric acid solution was then diluted with 2–3 times its quantity of water and poured into a saturated solution of caustic soda, ammonia or other alkali, so as to show an alkaline reaction. The titanium was this way precipitated as a hydroxide contaminated with some iron. In order to purify it from iron, two pounds of sulphate of sodium were added in crystals. The hydroxide of iron was this way converted into a sulphide and the color of the precipitate turned into a dark gray. The precipitate was thrown on the filter, washed twice with water to remove the superfluous sulphate of sodium; sulphurous acid was then applied for the purpose of decomposing the iron. The remaining hydroxide of titanium was then dried and ignited.

To the titanic acid was added four times its weight of crystalline oxalic acid and the mixture dissolved in as little hot water as practicable. A clear solution followed. The solution was evaporated in earthenware dishes or metallic dishes covered with lead to crystallization and cooled. The crystals were then drained from the mother liquor. To the titanium oxalate remaining in the mother-liquor a one and a half times larger quantity of acid oxalate of ammonium dissolved in hot water was added and the fluid concentrated to a syrupy condition. This then was allowed to solidify on cooling into a crystalline mass, containing besides titanium ammonium oxalate an acid titanium oxalate and some free oxalic acid.

In order to get 120 pounds of this crystalline mass the following ingredients were used:

30 lbs. rutile (80–90% TiO_2).
120 lbs. caustic sodium.
20 lbs. crystalline sulphate of sodium.
27 gals. hydrochloric acid of 30%.
96 lbs. crystalline oxalic acid.
38 lbs. crystalline ammonium oxalate.

The wash-water from the rutile flux contained enough alkali to precipitate the hydroxide from the hydrochloric acid solution. The oxalic acid regained by partial evaporization and crystallization amounted to about 25–26 lbs. This was only about 70 lbs. that had to be used in the continuous process of production.

The price of titanium in the ore was about the same as of solid tin metal, *i. e.*, too high if we take into consideration the complicated process of manufacture and purification.

H. W. Kearns and Dr. Barness applied on Dec. 5, 1896, for letters patent on titanium compounds, tannic compounds and similar compounds for coloring vegetable fibers (cotton, linen, jute, etc.) in raw or manufactured state during any stage of manufacture. Experiments made by Dr. Franz Erben[1] proved that a fiber treated with a tanning compound as a mordant and then subjected to the action of

[1] *Chem. Z.*, No. **14**, 1905.

titanium ammonium oxalate furnishes a saturated golden yellow color of great durability withstanding the action of boiling and washing. This coloring is preferable to that produced by chlorinated primalin and even the best sulphur colorings on the market. Dr. C. Dreher[1] is less enthusiastic concerning this tannin-titanium yellow in application to leather. However, Dr. Erben claims a favorable experience during nine years.

By the addition of small quantities of auranein G or O, acid orange or similar products the shades of yellow or orange can be modified at will.

The tannin-titanium base allows the improvements of many other colorings as for instance, red, green, blue, etc.

The man who did most for the introduction of titanium into metallurgical processes is Dr. Auguste J. Rossi.

In his contribution to the *Iron Age*, February 6 and 20, 1896, he summarizes his conclusions concerning titaniferous iron ores as follows:

1. These ores have been certainly smelted in Sweden for years without any difficulty.

2. Their metallurgical treatment for a certain number of years in England by Dr. Forbes, in a large furnace, has proved a perfect success.

3. Furnaces were run for years in the Adirondacks with these ores with excellent results.

4. The metal they yield, either as pig metal, iron or steel, possesses special valuable qualities.

5. These ores, which are found in large masses in many States of the Union, are almost invariably "Bessemer ores," and as such it is asserted have been used in Pennsylvania furnaces with great advantage.

6. When containing very large percentages of titanic acid (as much as 38 to 40 per cent. and even 48.60 per cent., like the ilmenite of Canada), and consequently a very small amount of iron (32 to 35 per cent. or less), their treatment though perfectly successful, metallurgically speaking, has not proved economical as to fuel. However, it would be more proper indeed to call an ore like the St. Urbain ore (Canada), which contains 48.6 per cent. of titanic acid, corresponding to 29.1 per cent. titanium and only 28.49 per cent. iron, a titanium ore than to call it an iron ore.

Dr. Forbes' treatment consists in adding to the titaniferous ores as fluxes, limestone and quartz or silica-bearing materials in such quantities as to form, with the titanic acid, a compound reproducing approximately a natural mineral of titanium, known to be fusible at a moderate temperature (3 of scale of Dana), the sphene or titanite, a silicotitanate of lime, containing about 35 per cent. of TiO_2, 25 per cent. to 33 per cent. of lime and 28–35 per cent. of silica. Dr. Rossi's method obviates the addition of silica, taxing the capacity of the furnace to excess. He introduces magnesia to a good amount into the slag by using a magnesia limestone, a dolomite. The alumina from the stone and ash of fuel and that very generally present as principal basic constituent of these ores furnishes all the amount which is required to form the tribasic compound with the magnesia and lime of the stone and the titanic acid of the ore. In the same manner that magnesia introduced in certain proportions into an alumina lime silicate renders the latter more fluid and fusible, the addition of magnesia to a titano-silicate of lime and alumina considerably increases its fusibility and especially its fluidity.

Dr. Rossi ran in a very small furnace, with a blast at a temperature not over 250 or 300° F. at the most, without any difficulty, slags of the following composition: SiO_2 16.63, TiO_2 34.66, CaO 26.03, Al_2O_3 7.26, MgO 10.27, FeO 7.12. Oxygen ratio 4.3 practically; actually 4.31. The ore smelted in that furnace contained only 1.5 to 2 per cent. silica or 20 per cent. titanic acid.

The conclusions arrived at by Dr. Rossi are as follows:

1. Titanic acid can form definite compounds, perfectly fusible, if properly fluxed, containing as much as 35 to 50 per cent. of titanic acid, with alumina, lime and magnesia as bases, and admissible as slags, in blast-furnace work. Larger percentages still, such as 65 per cent., can enter into a compound, and it remains fusible.

2. In running a furnace under special conditions of temperature and pressure of blast, no troubles have been experienced from titanium deposits.

That the smelting of titaniferous ores containing less than 20 per cent. titanic acid by means of an electric furnace is easier, than in an ordinary furnace, was proven by recent investigations, accounts of which were published in the technical literature.

We will refer here to a case not published yet. On December, 1906, Professor W. Borchers, of the Technische Hochschule at Aix La Chapelle, Belgium, prepared a mixture of titaniferous iron, sand of Java with lime and carbon in proportions calculated to produce a scorification of the gangue during the reduction to iron. A resistance furnace was used and a direct current of about 500 amperes

[1] *Faerber-Zeitung*, **8**, 295, 1902.

with a pressure of 50 to 60 volts was applied. The fusion of the mineral proceeded with the greatest ease. At the expiration of an hour and a half after the operation was started the temperature of the fused mass in the furnace was taken with the aid of Vanner's pyrometer. This temperature was found to be somewhat higher than 1900° C.

After this operation the slag was transferred to one crucible, while the metal was tapped into another crucible. Both crucibles were of course preheated. The slag was very fluid. The same day about three o'clock P.M. the contents of the cooled-down crucibles were examined.

A solid homogeneous ingot of metal weighing 1 kilogram, 620 grams, was found. The slag was black and had a vitreous fracture.

The analysis of the mineral was as follows:

Silicon		1.6	
Aluminum		traces	
Protoxide of iron	28.5 Fe =	22.18	57.15
Peroxide of iron	49.95 Fe =	34.97	
Oxide of manganese		0.98	
Lime		0.37	
Magnesia		2.35	
Sulphuric acid		0.69	S = 0.027
Phosphoric acid		0.096	P = 0.042
Copper		0.012	
Arsenic		0.005	
Titanic acid		16.00	
Loss on ignition		0.068	
		100.00	

The analysis of the metal was as follows:

Carbon, total	3.05
Manganese	1.52
Sulphur	0.01
Phosphor	0.11
Silicon	0.37
Iron	94.94
	100.00

There is, therefore, little doubt that titaniferous ores of less than 20 per cent. of titanic acid can be profitably smelted. All metallurgists agree that the qualities of the iron made from titaniferous ore and steel obtained from titanic pig metal are excellent. This fact gave Dr. Rossi the idea to use an alloy of iron and titanium made in the electric furnace as an improver of steel.

The addition of titanium to steel increases the transversal strength from 17 to 23 per cent. (average results given in pounds per square inch). Bars of one inch square, loaded at center, with 12 inches between support, were used for transverse strength tests. For tensile tests round bars 1 1/8 inches in diameter and from 18 to 24 inches long were used. The ferro-titanium added to the steel contained about 12 per cent. of titanium and from 6 to 8 per cent. carbon. About one pound to every 100 pounds were added in small portions. There seems to be no advantage in using a ferro-titanium containing more than 25 per cent. titanium. Titanium also increases remarkably the elasticity of steel.[1]

The function of titanium in steel consists in its high affinity for oxygen and especially nitrogen.

VACUUM EVAPORATION.

By P. B. Sadtler.

Received July 1, 1909.

It is a notable fact that, in this country at least, the knowledge of construction and operation of vacuum evaporating apparatus is very limited. There are a few industries, among which are the glucose, cane and beet sugar industries, where the engineers are in general pretty thoroughly familiar with this subject. Outside of these industries ignorance of the basic principles of evaporation actually frequently prevents engineers and superintendents from obtaining the best results. Those operating vacuum apparatus in their plants are prone to drop the subject completely as soon as their apparatus has been "broken in," only to take up the subject again when something goes wrong or when increased capacity must be installed to meet the demands of a growing business. Besides this class there is a long, though gradually diminishing, list of factory owners and others who either have entirely neglected to consider this important subject, or who, on doing so, have been frightened by some obstacle that seemed unsurmountable.

In this article will be discussed only the form of evaporator in which saturated steam is the heating medium as no evaporation can at present be done by direct fire so well as in the approved types of boiler, where the steam for the evaporator is made. The reasons why direct fire evaporation does not as a rule pay will be discussed on a later page.

A closed evaporator heated by steam coils has the following advantages:

1. Less steam is used because the apparatus is smaller and there is no exposed surface of boiling liquid, hence the amount of radiation and consequent loss of heat is reduced.

2. When evaporating under vacuum the temperature of the system is so lowered as to be nearly

[1] Dr. Rossi's contribution to *Cassier's Magazine*, Sept., 1905.

down to that of the atmosphere, with the result that the radiation loss is decreased. In other words, if a liquid is boiled in an open pan under atmospheric conditions the boiling point may be 220° F., or 150° above average atmospheric temperature. In a single-effect vacuum evaporator the average temperature may be 138° or 68° above atmospheric temperature. The radiation from the open pan would compare with that of the vacuum pan as 150° to 68° roughly.

3. The above considerations, however, are of little importance compared with the fact that a vacuum evaporator, either single- or multiple-effect, may be run by using, as a heating substance, the *exhaust steam* from engines, pumps, etc., thus enabling certain establishments to run an evaporator at practically no cost for steam.

4. There are many liquids which should be kept below the temperature 280° to 300° of high pressure steam coils, or even below atmospheric boiling point 212° F. Among these are such as sugar, glucose, sugar of milk, milk, glue, glycerine, etc.

5. Greater temperature differences may be attained in single effects, hence greater capacity for a given size apparatus.

6. When multiple-effect evaporators are used, the steam economy is increased to such an extent as to make the steam consumption run as low as 1/5, in some cases, of the actual amount of water evaporated from the liquid. There are some industrial concerns at present which could not operate and pay dividends without multiple-effect evaporators in constant use.

MULTIPLE-EFFECT PRINCIPLE.

The most primitive illustration of a multiple-effect evaporator is seen in an organic laboratory every day. Frequently a so-called volatile substance is put into a flask connected to a condenser and heated by a steam bath in which water is boiled. The vessel containing the boiling water is the first effect of a double-effect evaporator and the flask containing the low-boiling substance is the second effect. In the case of large scale work instead of boiling off a naturally volatile substance in the second effect, we boil off water whose vapor above it is kept at reduced pressure, thus making the water a relatively low-boiling substance. Thus in practice we have a succession of pans or effects, the coils of each one of which gets its heating vapor from the liquid of the preceding pan. The first pan of the series takes its heating vapor from the original source, the boiler or exhaust pipe of an engine; the last effect gives up its vapor to a condenser in which the highest vacuum is maintained. An important point to be borne in mind is, that every effect is the condenser that brings about the pressure reduction necessary for the operation of the preceding pan.

The most popular and universally serviceable evaporator is the triple effect, although they are in daily operation on a large scale up to sextuple effect. In fact, multiple-effect water stills have been operated in twelve successive effects. A definite determination of the number of effects to use to obtain the best economy when working on any given solution, is difficult to make. The best tests, of course, are those made on the large evaporators and as some expense and annoyance to the owner may result, the proper scientifically conducted tests are not carried out. One can, therefore, only go by the judgment of the designers and experts in this field in determining the best layout for economical multiple-effect evaporation.

STEAM CONSUMPTION.

Before discussing at length the factors governing the steam consumption in an evaporator, it is well to state several fundamental facts to be proven later:

1. *The number of effects used in an evaporative system does not necessarily bear any relation to the evaporative capacity of the system.*

2. *A given amount of water at the boiling point to be evaporated requires a corresponding amount of steam to evaporate it irrespective of the form or size of the vessel in which the evaporation is accomplished.* Speaking broadly, a pound of water evaporated requires that a pound of steam be condensed in a single effect.

3. *The capacity of a heating surface is dependent on the temperature of the steam and not the pressure resulting therefrom.*

4. *An evaporator should not be considered as a heat engine, as it does no external work.*

To get the best idea of the heat transactions in the evaporator, we should consider one effect at a time. Also, for simplicity, assume that the effects are of the same construction and bear in mind that each one is the condenser to produce the vacuum in the preceding effect. For every pound of dry steam entering the coils of the first effect, there is one pound of vapor produced by

the evaporation of the solution which we assume enters at the boiling temperature. As only a fraction of the total amount of water is to be evaporated in the first effect, the solution passes partly concentrated into the next effect. But as a lower pressure, and consequently lower temperature, is being maintained in the second effect, the solution passes in a superheated condition to the next effect, where a certain amount of evaporation takes place, due to the lowering of the pressure. Therefore in the second effect we have to expect the evaporation of another pound, plus increment due to the changing part of the heat of the liquid into heat of vaporization. Likewise in the third effect there is produced evaporation to the extent of a pound, plus two increments. In other words, the latent heat of a pound of steam is transferred through the heating surfaces of one effect after another, the amount of steam being, however, gradually increased by the spontaneous evaporation of the solution passing from one effect to another successively in a superheated condition. Finally this heat passes into the cooling water of the condenser and is lost. If we were to assume that there was no radiation of heat from the system and that pure water were being boiled, the above conditions would be always true and, in a sextuple effect, a single pound of initial heating steam would accomplish the evaporation of between six and seven pounds of water.

In actual fact, however, we have to contend with the consumption of heat in two other directions:

1. In concentrating any solution we have to accomplish the partial separation of a liquid from a solid. There is, of course, a certain solution pressure against which we must work, and the actual amount of energy expended in this way is measured by the free energy of the chemical reaction of solution. This is not considerable when we concentrate to ordinary density. Hence it may be said that *the total reversible energy expended in evaporation is equal to the free energy of reaction.*

2. There is a radiation loss from each effect depending on the number of effects, their temperature with respect to atmospheric temperature, the amount and quality of the insulating covering used and other conditions such as degree of exposure of the apparatus to the weather.

These losses are cumulative from one effect to another so that where a solution has boiling points appreciably above that of water, it is not economical to attempt the operation of more than a limited number of effects.

DIAGRAMS.

To illustrate several cases of heat transactions obtaining in an evaporator:

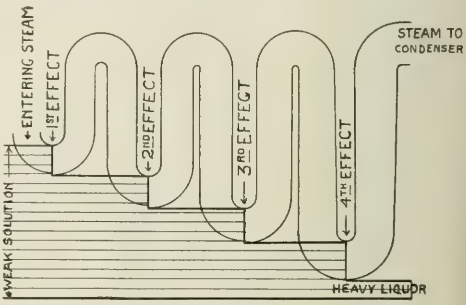


Fig. 1.

Figure 1 shows a multiple effect heat diagram similar to that of Hausbrand for pure water in a quadruple-effect evaporator, where it is assumed that the difference in temperature from one effect to another is infinitesimal and where water enters at boiling temperature and the vessels do not radiate heat.

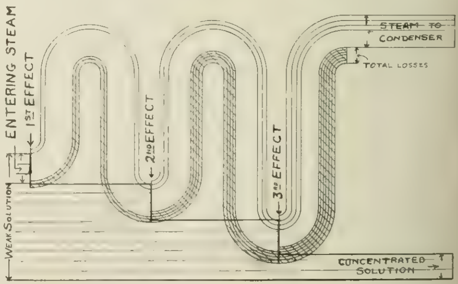


Fig. 2.

Figure 2 shows a heat diagram for a triple effect where the assumptions are made that the solution enters at atmospheric temperature, the solution has an appreciable excess in boiling temperature over that of water, and there is an appreciable temperature difference from one effect to another. The white areas represent the steam condensing and causing evaporation; the shaded areas represent the heat and energy losses as expressed in steam. The areas shown are not

definitely measurable or calculable, but merely in the diagram show the tendencies existing in an evaporation system.

The heat transferences taking place in a multiple effect are altered in character to a great extent by the method of feeding the solution to be concentrated and the method of preheating if such is necessary. There are four ways of feeding the solution to the evaporator:

1. The dilute solution is fed entirely into the first effect and passes successively from one effect to another at higher and higher concentrations.

2. The dilute solution is fed in equal amounts separately into each effect, and boiled in each at the same concentration.

3. The dilute solution is fed entirely into the last effect and passes back to the first effect, a method known as running backward.

4. The dilute solution is pumped into the whole evaporator before starting and boiled in batches.

While inquiring into the relation, merits and advantages of these methods, let us consider at the same time the methods of bringing the dilute liquor to the boiling point and the bearing of these methods upon the heat transactions.

While in many cases a recently completed chemical reaction or industrial process leaves the dilute solution at a temperature approaching the boiling point, such as we find to be the case in certain mercerizing work, in electrolytic soda work or packing house rendering, there are other cases such as brine evaporation or sugar evaporation where the most efficient process necessarily includes the preheating of dilute solutions. In general, it may be said that running a comparitively cool solution into an evaporating apparatus decreases its efficiency and interferes with proper operation.

The usual method of preheating in running a multiple-effect concentrating evaporator as mentioned, in case 1, above, is to employ a steam heater to preheat the solution entering the first effect by the use of live or exhaust steam. Frequently it is assumed that it is quite sufficient to turn on a little extra steam and run the solution cold into the evaporator. When this is done a portion of the heating surface of the effect, into which the cold solution is run, plays the part of a preheating apparatus. An evaporator is an expensive article to use as a preheater.

Where evaporating at equal densities, as in the second case above, there may be attached to each effect a countercurrent heater in which the water of condensation, flowing from an effect, partly preheats the liquor being pumped into the effect. It can readily be perceived that the amount of heat that can be transferred to the solution from the water of condensation is insufficient to bring the former up to the required boiling point. This method is only applicable to precipitation work, as in multiple-effect salt evaporators.

When "running backwards" preheating is not often the practice as the boiling point of the last pan, the one which the solution enters, is not very high and the step up in temperature from one pan to another is not very great. This method has the advantage, other things being equal, that in the pan with the densest solution, there is the highest temperature, which tends towards better circulation and consequently higher efficiency. In using this method it is necessary to pump the liquid out of one effect into the next. The fact that steam is used to do the pumping need not have much bearing on the question, as it must be borne in mind that the exhaust steam from pumps is available for evaporation purposes.

The total consumption of heat in a multiple effect is composed of the energy consumed in actual separation of the liquid and the solid in solution; the radiation of heat from the walls of the vessel; the heat passing away in the circulating water of the condenser; and the heat passing away in the condensation water. In a test on an evaporator these can all be determined by actual measurement except the energy of evaporation and the radiation loss. There is always considerable doubt as to just what the latter amounts to in various types of evaporator and with various coverings. It is possible to measure it by special test, though this is rarely done. The energy of evaporation may be calculated for certain solutions and simply depends on a formula which may be derived from the gas laws.

It is shown by Nernst in the last edition of his "Theoretical Chemistry" that the energy expended in evaporation is

$$K \times R \times T \times (C - C'),$$

where R = the gas constant, T = the absolute temperature, C′ = initial concentration, and C = the final concentration both expressed in mols. of salt per mol. of water. K is a constant quantity for any given substance in solution. For certain inorganic salts these constants have been deter-

mined, being derivable from the vapor pressure curves.

EFFICIENCY AND EVAPORATIVE CAPACITY.

A heat engine is an apparatus that transforms a portion of the heat received into dynamic energy. An evaporator is not a heat engine, therefore, but if the assumption be correct that solution is a chemical combination of solvent and solute, an evaporator transforms heat into chemical energy. When following this analogy between a heat engine and an evaporating system, we find that as a matter of fact the efficiency or the quantity $\frac{Q - Q'}{Q}$, where Q is the heat entering and $Q - Q'$ is the heat transformed in chemical energy, is very low. The heat disposed of through other channels is very great. For instance, the latent heat of the entering steam eventually finds its way in large part into the circulating water of the condenser. Therefore, it will readily be seen that if, as we have shown above, this energy demanded for evaporation is entirely dependent upon absolute temperature and degree of concentration, *no one type of evaporator has more efficiency than another, but the efficiency is entirely dependent upon the solution and its attendant physical conditions.*

This matter of efficiency is noted here as there is an erroneous conception among some evaporator engineers as to the meaning of the word efficiency. It has been the practice among some to speak of the relative amount of evaporation per unit area of heating surface as the efficiency of an evaporator. The difficulty with using the term efficiency where the term capacity or duty would be more applicable, is that it leads those unacquainted with the principles to the idea that greater or less consumption of heat obtains in different types of evaporators. In different types of evaporators the evaporative capacity does vary considerably, but it is not the purpose of this article to discuss this side of the question, as the relative merits and demerits of different makes of machinery demand a separate article.

Before discussing the subject of capacity and the calculation of heating surface, it is well to approach the subject from the point of view of transmission of heat through the heating surface.

HEAT TRANSMISSION.

Heat transmission is measured by four fundamental factors, namely, temperature, weight, space, and time. To be more specific, the common combination of units, in which we express heat transmission, is British thermal units, per square foot, per hour. Therefore, the coefficient of the heat transmission of a medium would be the figure which gives the number of British thermal units passing per hour from a warmer to a colder substance through one square foot of the medium for which we desire the coefficient.

It will readily be seen that the ability of the medium to transmit heat in a greater or less degree is governed by the following factors, namely, nature of the material, thickness of the medium, difference in temperature of the warmer and the colder substance. Hence, we have

$$h = k\frac{(t - t')}{d}m,$$

where h is heat transmitted, m is the time during which transmission takes place, d the thickness of the transmitting medium, $t - t'$ difference in temperature, and k a constant dependent on the nature of the material.

From the above we see that

$$k = \frac{d \times h}{(t - t')m},$$

whence we are able to determine a constant k for any material by determining d, h, $(t - t')$, and m for one square foot of heating surface. For practical purposes, where for a given material the limits of the factor d are quite narrow, this is omitted and the constant becomes

$$k = \frac{h}{(t - t')m}.$$

In the case of the transference of heat from one substance to another, for evaporative purposes, we have several possibilities: that of heat passing *from* a liquid, *from* steam, or *from* other gases; also heat passing *to* a body of liquid or *to* a film of liquid.

In evaporation work the case of heat passing from a liquid is not of very wide importance. Other things being equal k would be high in this case, but the difficulties involved in this method of heating necessarily outweigh those of steam heating. A high-boiling liquid may be heated and made to pass through heating tubes, giving a high transference constant, but the velocity necessary for its passage through the tubes is great enough to make the idea unworthy of consideration.

In the case of saturated steam there is not the

same necessity for an appreciable velocity directly in relation with the walls of the heating tubes, though this is very desirable. Unlike the case of direct heating, the effect is obtained by the latent heat of vaporization. Although the heating of the liquid is not due to difference in temperature between the steam and the liquid being heated, there must be a quite appreciable difference in temperature to make effective use of the latent heat. The larger the difference in temperature the greater is the heat transmission of the metal walls.

As water dissolves air to a small extent the steam from the boiler always contains air in greater or less amount. This air tenus to lessen the heat transmission so that it will be found in practice that better boiling takes place in the heating coil, where the velocity is considerable.

It can readily be seen, therefore, that the presence of *air in the heating steam is detrimental.* Just as air reduces the heat transmission so also does the water produced by condensation of the steam. The heat conductivity of water is far below that of a metal, so that a *steam coil containing a layer of water is not fully effective.*

The usual case of heating by other gases than steam is direct firing of boilers or evaporators, or the utilization of waste heat from furnaces, incinerators, etc. Here the transmission of heat is due to the difference in temperature and *the velocity of the gas.* It will readily be seen that if a body of cooled inert, non-condensable gas stays in contact with the wall of the heating surface the efficiency of the locality where that takes place is greatly reduced. On the other hand, in the case of steam the pressure back of the heating steam is cause for constant supply of the steam, which gives up its latent heat to the wall of the heating surface. A non-condensable gas, to be equivalent in effect to a condensable gas, like steam, must be led against the heat-transferring wall with considerable velocity to cause the rapid removal of cooled gas and prevent lodging of cooled gas in any small corners or devious places.

Very little can be determined as to the theoretical side of the transmission of heat *to* different solutions and solids. In general, it may be said that the completeness of the circulation of the liquid, the consequent rapidity of the disposal of the steam formed at the contact between the liquid and the heating surface, and the degree of mobility of the liquor are the chief factors for consideration here. More can be said later of interest and of value from a practical standpoint.

The heat transmission may be said to be greater when the liquid is in contact with the heating surface in as thin layers as possible. This is accomplished by allowing the liquor to spray or trickle over the heating surface or by bringing the liquor in contact with the surface in the form of a foam. When a film is in contact with the heating surface the evaporation may be said to be local; hence there is a local cooling tendency and consequent greater temperature difference between the liquor heated and the heating gas. This it will be seen will increase the heat transmission.

There has been an erroneous notion prevalent among some engineers that the evaporative capacity of a heating surface of any given form and area is inversely proportional to the thickness of the wall of the heating tube and proportional to the heat conductivity of the particular metal used. This idea is quite wide of the mark, as decided by results. If two otherwise equal evaporators be installed in which one has heating tubes of 20-gauge and the other 15-gauge, such a theory would require that the latter would have half the evaporative capacity of the former, 15-gauge being twice as thick as 20-gauge. As a matter of fact the difference due to this variation in thickness is negligible. However, the difference between the evaporative capacities of two heating surfaces of different metals is measurable if two metals of widely different conductivities be chosen, but even then the difference is not great as might be supposed.

Kent gives, among others, the following conductivities:

Silver	1000
Copper (rolled)	845
Iron (wrought)	436
Steel	397

In spite of these figures the evaporative factor of copper tubes is only 10 per cent. to 15 per cent. greater than that of steel tubes.

To explain these facts we must consider that the resistances of the metallic wall to the passage of heat are threefold, namely, (1) resistance of entry of heat into the metallic wall, (2) resistance to passage through the wall, (3) resistance to the exit from the metal to the boiling solution. Let these resistances produce conductivities a, b, and d, respectively. Let C represent the evaporative factor of the metal by experiment.

$\frac{1}{C}$ = total resistance $= K\left[\frac{1}{a} + \frac{1}{b} + \frac{1}{d}\right]$ or the sum of the three resistances.

$C = \frac{1}{K\left[\frac{1}{a} + \frac{1}{b} + \frac{1}{d}\right]}$ where K is an arbitrary constant. Conductivity a is effected by the ease with which the steam for heating is carried off and also the velocity of the steam; conductivity b is constant for a given metal; conductivity d is dependent upon the solution being handled, its boiling point, mobility, scaling properties, etc.

CALCULATION OF HEATING SURFACE.

The amount of heating surface necessary in an evaporator to be used for any given class of work depends on the following factors: 1. The amount of water to be evaporated, (2) the number of effects desired, (3) the initial steam pressure, (4) the boiling points of the solution to be evaporated, (5) the evaporative factor for a given type of machine, and for a given solution to be evaporated,

In calculating the amount of water to be evaporated, it is merely necessary to obtain from tables or analysis, the per cent. of solids in the dilute and the concentrated liquor. From this we can obtain the amount of water to be evaporated. When the number of effects in which the evaporation is to be done is determined, a calculation should be made of the water evaporated in each effect and from that, what the concentration should be maintained at, in each effect. When these concentrations are known the corresponding boiling points should be found from a good table of boiling points or by experiment, or a curve such as shown in Fig. 3 for certain grades of caustic

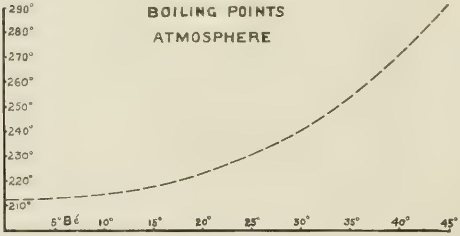


Fig 3

soda washings may be used. The *degrees of excess boiling* temperature is the total of each of these boiling points less 212° F. In other words, if the boiling points in three effects of a triple effect are respectively 214°, 220°, and 236°, the excess boiling temperature is (214 — 212) + (220 — 212) + (236 — 212) = 34°.

From the steam tables of pressure and temperature the *total temperature range* should be found. Or it will be found very useful to use a curve as shown in Fig. 4 where the pressures and

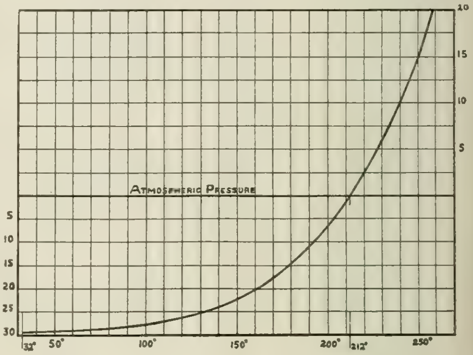


Fig. 4.

temperatures are plotted. Readings from such a plot compare favorably in accuracy with actual steam gauge readings on the evaporator. This temperature range then equals the temperature corresponding to initial steam pressure minus the temperature of steam pressure corresponding to vacuum maintained in the last effect.

The *evaporative factor* is a constant quantity. The total temperature range less the excess boiling is the *effective range*. This divided by the number of effects equals the *average effect difference*. The evaporative factor is derived from experience and from operative tests on the type of apparatus best adapted and on the given class of liquor to be evaporated. Probably the same factor would hold, for instance, on all submerged tube evaporators of the general type of those under discussion and would hold for either caustic soda solutions or carbonate of soda solutions, scaling conditions, etc., being otherwise the same. In fact the same constant quantity could be used, and has been used, in designing evaporators for a large range of inorganic chemical solutions, such as sodium chloride, sodium hydrate, sodium carbonate, sodium sulphate, sodium phosphate, sodium acid phosphate, sodium thiosulphate, potassium chloride, potassium hydrate, ferrous sulphate, calcium acetate, etc. However, in cases of tannic acid, sugar, glucose, glycerine, black liquor, or resinate of soda, packing house tank water, garbage

tank water, etc., somewhat different conditions obtain and the factor varies. The factor also differs slightly for different materials for the heating surface, that for copper or aluminum being distinctly higher than that for iron.

To specify the units on which this factor is generally based we might say that it is expressed as gallons of water evaporated, per square foot of heating surface per degree difference in temperature per hour.

If C = evaporative factor
E = average effect difference
W = gallons evaporated
T = time in hours during which evaporation proceeds
S = square feet of heating surface

$$C = \frac{W}{E \times T \times S}.$$

Hence, if we find from experience or trial tests the value of C and we calculate E and W, as explained above, it is easy to obtain the required heating surface.

The successful designing of an evaporator is dependent first on the recognition of certain chemical and physical facts relating to the substance to be evaporated; second, on whether or not due regard is paid to certain thermal and thermodynamic principles involved; and third, on certain mechanical features that arise in the construction. It is not to be supposed that either an engineer, familiar with the best boiler practice, or a chemist, familiar with laboratory or open-pan evaporation in the works, could successfully design a multiple-effect evaporator. But certain facts in regard to design should certainly aid either a chemist or engineer in procuring the proper design or making a purchase.

As the principal purpose of an evaporator is to concentrate a solution of some sort, it will be readily seen that the chemical and physical laws governing concentrated solutions will be of importance. These are only known qualitatively and the quantitative laws which govern the chemistry of dilute solutions are inapplicable.

As most measurements of the concentration of solutions in the works are made with a hydrometer we generally speak of concentrating between certain limits in degrees, Baumé, Twaddell, Brix, salinometer, or specific gravity. It is, therefore, necessary to obtain or devise tables or curves showing the relation of these units of concentration with the percentage of solid matter in solution. The purpose of this is to obtain accurate information as to the actual amount of water that is going to be evaporated in a unit of time. This is especially important in cases where the vapor arising from the solution is the source of heat in the succeeding effect of the evaporator.

Of equal or greater importance, is a table or curve for a given solution which shall accurately show the relation between the boiling point of the solution and its concentration. It has been shown above, that the boiling point of a solution at any period of its progress through the evaporator has a direct bearing upon the size of the evaporator. A boiling point curve is generally obtained by taking simultaneous readings upon a hydrometer and thermometer, while boiling a solution actively under atmospheric conditions. This may best be accomplished in a laboratory where accurate means of determination are provided. After this curve is obtained a correction should be made for temperature at boiling to bring the hydrometer readings to the same temperature standard.

In cases where a substance is intended to precipitate from solution, during the process of evaporation, there should be used in conjunction with the above table also a table of solubilities of the substance at different temperatures.

The thermodynamic data necessary consist of the regular steam engineer's tables, showing the relations between temperature, pressure, heat of liquid, heat of vaporization, etc.

There are other chemical and physical data of which account must be taken in designing. The more information obtainable in regard to possible incrustation and scaling of heating surface, the clearer will be the idea as to what mechanical features to introduce for the removal of scale and as to what excess capacity to allow for this contingency. As in boiler practice, one of the greatest sources of annoyance is the deposition of gypsum on the tubes. This annoyance is encountered in the salt industry especially; on account of the peculiar solubility relation of gypsum, it is found more expedient to evaporate at low temperature with large heating surface, thus minimizing the scale. Another similar case is that of soda washings in pulp mills, where cooking liquor is evaporated for soda recovery. If the lime used in the course of the process is high in silica and alumina, these find their way to the evaporator and deposit in a dense fibrous scale. If such possibilities as

these are to arise, it is found expedient to have the heating surface in excess of the calculated area and easily removable from the evaporator for cleaning purposes. Moreover, it should be removable where corrosion is expected. There are some chemical solutions which corrode iron at the higher temperatures but are inactive at lower temperatures. In these cases the heating surface bears the brunt of the destruction in the evaporator.

Another important question is, as to the nature of a solution's activity under boiling conditions. In other words, does the boiling solution tend towards entrainment or foaming, or spattering? These points must be known beforehand, as they decidedly influence the proportioning of the evaporator.

PROPERTIES OF LIQUIDS AS AFFECTING CONSTRUCTION.

In some industries the multiple-effect evaporator is among the largest and most expensive of the installations in the factory. Where a large evaporator is to be built for constant use, great attention should be paid to details of its design and construction. The liquids commonly evaporated in any quantity can be divided into two classes: those that foam on boiling and those that do not. It may be said in general that a liquor that entrains (or sprays and passes over with its vapor) does not foam, and a foaming liquor does not entrain. Also it is noticeable that solutions of alkaline reaction tend to foam while those of acid reaction tend to entrain. Most sugar juices and glucose come under the latter class. To provide against losses due to entrainment in an evaporator there are to be mentioned such methods as the use of baffle plates, catchalls, and high-vapor dome. The so-called film evaporators are subject to the difficulty in this respect that the vapor space allowed is invariably small and from the time a portion of the vapor leaves the boiling solution it carries with it a large amount of spray in suspension in its rapid passage through tortuous channels of small cross-section. The simpler types of evaporator whose construction is more like that of a tank are open to the objection often, that the vapor is drawn off from a dome directly over the boiling surface. In these simpler types of evaporators it can be arranged easily to have the sectional area large enough to make the rising of the vapor slow and the height of the dome sufficient to cause practically all the entrainment to drop back. In order not to cause any inversion or possible discoloration in the sugar juices it has been found advisable to have as little as possible of the juice in actual transit through the apparatus. This is accomplished by two principal methods: one by having a rather shallow bank of tubes in which the tubes are packed in the tube sheets as closely together as possible; another by spraying the juice over the heating surface, collecting it underneath and pumping it back again to the spray. This latter method rather subjects the juice to loss from entrainment, unless the vapor dome is extremely high.

In dealing with soda solutions the problems arising are of a very different nature from those in sugar work. Under the head of soda solutions we may include, among other important cases, the evaporation of sodium carbonate, sodium phosphate, pure caustic soda and caustic soda containing brine (electrolytic), black liquor (pulp-mill), mercerizing soda, etc. Except in the case of the more concentrated liquor of the last effect these are all more or less foamy when boiling. The use of baffle plates alone does not accomplish the prevention of loss when foaming takes place. It has been found that the only sure and efficient way to deal with foam, that is to cause it to subside, is to break the individual bubbles by application of heat. Hence the evaporator should be built in such a way that the heating surface is in a high bank above the level of the liquor evaporating. On operating the apparatus it may easily be found by trial what is the proper level of liquid shown in the gauge glass to prevent the foam from rising much above the top of the tubes and yet keep the tubes covered. About the most difficult liquors to handle in this respect are those in pulp-mills or mercerizing plants. In these cases it is necessary to have the heating tube bank almost half the height of the evaporator.

In salt industries there are two main difficulties which have to be met by the designer of an evaporator: first, the salt has to be removed from the apparatus constantly as it precipitates from solution; second, scale that deposits upon the heating surface has to be removed periodically. In order to render the removal of precipitated salt simple and rapid it has been found best to construct the evaporator with a hopper-shaped bottom having

either one or two hoppers leading through a valve at their lowest point into a receiver where the salt is separated by draining through a false bottom. Another method consists in precipitating the salt continuously down a barometric leg under the evaporator, draining it and conveying it from the bottom by a closed elevator. This latter method is generally most efficient when working on a very large scale. In salt evaporation work, shut-downs are frequently necessary every day because of the constant deposit of gypsum upon the heating surface. This happens to such an extent that the evaporative capacity of the apparatus is reduced to a point where it no longer pays to operate. Ready means of access should be provided so that the heating surface may be thoroughly cleaned, or arrangements should be made for rapid pumping and boiling of suitable chemicals for the disintegration of scale.

There are certain acid salts which require special construction in order to line the evaporator with lead. This lead lining has never been done on a very large scale. In principle it consists in first pickling in sulphuric acid the plates of the machine, these being built with flanges that can be bolted together. The pickled surface is then given a tin coating. A sheet of lead of the proper thickness and size is coated with tin. The two tinned surfaces are laid together and the lead hammered to fit. Then the lead is "sweated" on by heating the iron from the outside to the melting point of the tin plating, which is lower than that of the lead. In this way the lead lining becomes attached to the steel by a homogeneous weld. Where the flanges are bolted together the contact of the two lead surfaces generally prevents leakage, but can be made more sure by the process of lead-burning.

It is generally most expedient to work out the size of the heating bank from the amount of heating surface determined upon before deciding upon the general dimensions of the shell of the evaporator. The first thing to consider is the bore of tubing to be used. If we are dealing with a vertical type of evaporator where the tubes are expanded into two horizontal tube sheets, the bore of the tubing is determined by the nature of the liquid which is to be evaporated in them and the magnitude of the work to be accomplished. In the case of the horizontal type of evaporator where the steam is in the inside of the tubes and the liquor on the outside, there has been found a ratio of length to diameter for which the steam that condenses within gives a maximum evaporative capacity. If the tubes are too long and constricted, the steam will condense before it can pass to the far end of them, and a certain amount of heating surface is thereby wasted. It is usual to decide upon a certain length and diameter of tubing, however, arbitrarily from experience. It is then easy to decide, from the nature of the solution and taking into account the temperature differences and rate of evaporation, the proportioning of the heating bank. In a vertical effect when the length, diameter and centre line distances are decided it is merely a question of filling a certain number of tubes in the minimum sized circle.

Tubes may be attached to the tube heads or tube sheets by one of two methods, that of packing them in or expanding them in. To pack the tube in the tube sheet well, the hole in the sheet must be countersunk conically to admit of the forcing in of the rubber packing. This rubber ring is pressed in by a metallic place so that it is forced against the hole in the tube sheet and against the tube. This plate is held to the sheet by a stud bolt, and is arranged to hold down four, six or eight packing rings simultaneously.

When tubes are expanded into the tube sheet, it is expected that they are to be removed at no time during their life, whereas packed tubes can be easily removed, cleaned and repacked. Tubes expanded into the tube sheets properly make a perfectly steam-tight joint for almost any pressure or vacuum. The tubes are extended through the sheets a slight distance and are beaded over and are expanded by a special tool for this purpose. The Prosser expander rolls a corrugation in the tube, just inside of the sheet and beads it outside the sheet. In this way the sheet is braced against pressure from within or without. The Dudgeon expander rolls the tube flat against the side of the hole and beads it over on the outside. This method is not as effective in results, but is less of a strain on the metal of the tube.

I hope at a later date it may be possible to go more deeply into the practical side of this subject, presenting as far as possible the best solutions to problems arising from day to day.

Swenson Evaporator Co.,
Chicago.

RECOVERY OF GLYCERINE BY THE TWITCHELL PROCESS COMPARED WITH THE RECOVERY OF GLYCERINE BY WASTE SOAP LYE METHODS.

By O. T. Joslin.

Received July 17, 1909.

As the Twitchell process has now been used on a manufacturing scale for ten years in one factory, for eight years in a half dozen or more factories, and in many others for a lesser period, there are ample figures to show very closely what advantages this process possesses over waste soap lye methods.

I will give a schedule of the operations involved and the costs and credits of the two methods.

Cost of Twitchell process plant to work 8000 lbs fat per day including glycerine evaporating plant	$2800.00
Cost of waste soap lye glycerine plant for 8000 lbs. fat per day	3900.00

Cost of Working 8000 Lbs. Fats or Oils in the Kettle by the Old Process.

Cost of boiling kettle through six changes, killing change, three glycerine changes, one strengthening change and one settle; steam, labor, etc., at $2.00 per change	$12.00
Cost of salt for three changes at 1/4 c. a lb., 1920 lbs. salt equals $4.80 four-fifths of salt recovered, gives salt cost	0.96
Cost of saponifying with caustic 18.58 per cent. of 60 per cent. caustic at $2.10	31.20
	$44.16

All other costs will remain same in both instances.

Cost of Working 8000 Lbs. Fats or Oils by the Twitchell Process.

Steam (coal at $3.00 per ton)	$1.00
Labor	1.00
Sulphuric acid (at 80 c. per 100 lbs.)	0.80
Barium carbonate	0.75
Reagent (at 15 c. per pound)	7.20
	$10.75
Expense (insurance, repairs, deterioration) 20 per cent. of cost of Twitchell plant, $1450.00 equals $290.00 for the year, divided by 250 days, equals	1.16
	$11.91
Cost of working 100 lbs. of stock	$0.1488

Entire Cost of Working 8000 Lbs. Fats or Oil by Twitchell Process and through the Kettle.

Twitchell process cost	$11.91
Cost of boiling kettle through four changes, killing change, one salt change, one strengthening change and one settle, steam, labor, etc., at $2.00 per change	8.00
Cost of 640 lbs. salt at 1/4 c. a lb. (no salt recovered)	1.60
Cost of alkali for saponifying:	
95 per cent. soda ash at 1 c. for 48 per cent.	17.65
5 per cent. soda caustic at $2.10 for 60 per cent.	1.56
	$40.72

Cost of saponifying with 95 per cent. ash and 5 per cent. caustic $19.21, or $31.20 − $19.21 = $11.99 or 15 c. per hundred lbs. stock saved by soda ash saponification.

Cost of Working Waste Soap Lyes from 8000 Lbs. Stock Per Day, 18,000 Lbs. Lye.

Acid	$ .50
Chemicals	1.00
Labor, two men all day	3.50
Expense (insurance, repairs, deterioration): 20 per cent. of $3900.00 equals $780.00 per year of 250 days, equals $3.12 a day	3.12
Steam for heating and handling lyes aside from evaporating	1.50
Steam for evaporating equivalent to 1500 lbs. coal at $3.00 a ton	2.25
Water, 26,000 gallons per day at 10 c. a 1000 gallons	2.60
	$14.47

Maximum amount of glycerine obtainable by waste soap lye methods is 8 lbs. absolute glycerine per 100 lb. neutral fat.

On stock containing 5 per cent. free fatty acids the amount of glycerine would be reduced to 7.5 lbs.

On 8000 lbs. this gives 600 lbs. at 13 c. a lb., $78.00.

Cost of Working Twitchell Process Glycerine.

8000 lbs. stock per day 5200 lbs. glycerine water	....
Lime	$0.05
No other expenses of treatment.	
Labor, one man a day	1.75
Expense (insurance, repairs, deterioration): 20 per cent. of 1350 equals $270.00 per year of 250 days	1.08
Steam for evaporating, 433 lbs. coal at $3.00 a ton	0.65
Water, 12,500 gallons per day at 10 c. a 1000 gallons	1.25
	$4.78

Maximum amount of glycerine obtainable, 95 per cent. of the glycerine in the fat, at 5 per cent. free fatty acids in the fat, would give 9.5 lbs. glycerine in the water per 100 lbs. stock and allowing 5 per cent. loss of glycerine in process of working up the glycerine water, would give 9 lbs. of absolute glycerine on the fat. On 8000 lbs. this gives 720 lbs. glycerine at 14 c., a lb. equals $100.80.

Old method	Cost.	*Twitchell process*	Cost
Making soap	$44.16	Making soap, including cost of Twitchell process	$40.72
Glycerine recovery	14.47	Glycerine recovery	4.78
	$58.63		$45.50
	45.50		

Profit of $13.13 due to manufacturing

Value of glycerine recovered by Twitchell process	$100.80
Value of glycerine recovered by waste soap lye process	78.00
Profit due to glycerine	$22.80
Profit due to manufacturing	$13.13
Profit due to glycerine	22.80
Profit on 8000 lbs. stock	$35.93
Profit on 100 lbs. stock	0.45
Additional profit per day due to the Twitchell process	$35.93

The advantages mentioned above are due to the following differences between the two processes:

First, the fact that almost all the glycerine is separated from the stock before it goes to the kettle avoids the loss due to glycerine remaining in the soap, and the loss due to the complicated and lengthy process necessary in recovering glycerine from waste soap lyes.

Second, the fact that Twitchell process liquors contain from 15 per cent. to 20 per cent. glycerine, while waste soap lyes run between 3 per cent. and 5 per cent, results in a saving of glycerine on account of the very much less evaporation required in the case of Twitchell liquors.

Third, the greater strength in glycerine of the liquors reduces the amount of water to be removed by evaporation to 1/4 or 1/6 of what is necessary to be removed from waste soap lyes. This of course makes a commensurate reduction in the amount of steam, condensation water, labor and time, and consequently expense.

Fourth, the absence of salt from the glycerine liquors is a most important advantage, which, while readily recognized by all who have used the waste lye methods, is not fully appreciated until both methods have been used and compared.

The presence of salt in glycerine lyes makes a larger, more complicated and more expensive evaporator necessary. It also causes the evaporator and all other parts of the plant to corrode and wear out much more rapidly. It necessitates salt strainers and an extra pump, and a considerable extra amount of labor, while some glycerine always remains in the salt, and sometimes much. This glycerine salt should, of course, go back to a kettle which is having the glycerine extracted from it, but it does not always go this way, and even when it does there is some loss of glycerine anyway, as mentioned above.

Fifth, the much greater purity of Twitchell liquors over waste soap lyes makes several additional savings. The treatment necessary is simple and cheap in the extreme, both in regard to materials and labor required. The waste material separated as a result of this treatment is so much smaller in amount that there is a saving of glycerine here, as such residues can never be completely freed of glycerine.

The absence of salts and other impurities causes the glycerine liquors to evaporate much more easily, with a consequent saving similar to that accruing from the less amount of water to be removed as above mentioned.

Sixth, a crude glycerine containing 90 per cent. of glycerine can be obtained with much more ease and certainty than an 80 per cent. crude can be obtained from waste soap lyes. This makes an appreciable saving in drums, labor of handling and freight.

Seventh, the greater strength and purity of the crude glycerine puts it in a special class known as saponification crude. Saponification crude should have 88 per cent. of glycerine or more and 5/10 per cent. or less of ash. This standard is easily reached by Twitchell liquors. Saponification crude usually brings one cent a pound or more on the absolute glycerine contained than soap lye crude. This advantage accrues to the producer when the glycerine is sold as crude. If a plant distils its own crude it derives the advantage in the form of greatly increased capacity of a still of a given size for this crude over waste soap lye crude, less steam and labor and a greater yield, and a purer product with one distillation, as C. P. glycerine can be made with one distillation. Finally, I never heard of any one finding glycols in Twitchell glycerine.

Another important advantage is the saponification with sodium carbonate instead of sodium hydroxide. This makes a saving of 14 or 15 c. on every hundred pounds of stock saponified in this way. For a good many years there was a strong, prejudice against the sodium carbonate saponification. This prejudice was without reason and during the last few years it has almost entirely disappeared. It is a fact that the soap made by carbonate saponification is the same in every way as soap made from the same stock by caustic saponification. There is also no difficulty in making the carbonate saponification in the kettle, except the slight difficulty which always accompanies a new method of procedure. This fact was first demonstrated in Europe, but is now accepted by all the experienced American soapmakers.

There are in addition several lesser advantages which the Twitchell process possesses. One is the decrease in the odor which the process occasions in the case of many strong smelling stocks. In some cases this becomes a matter of great importance. Corn oil for instance was formerly of little value for soap and was but little used for this purpose,. but since the introduction of the

Twitchell process its use has been greatly increased, as the process diminishes the odor so greatly, that corn oil becomes available for soap and soap powder, when worked by the Twitchell process, while it is entirely out of the question when not so worked. The process removes the heavy disagreeable odor of this oil to such an extent that it is not noticeable in the finished soap product, even when unperfumed. The odor of animal fats is also greatly diminished and this is a great advantage in the manufacture of toilet soaps.

There is a class of soaps, known as cold-made or half-boiled, in the manufacture of which the glycerine has heretofore been lost, as it remained in the soap. There are several special reasons why soaps of this nature should be made, and they are made in large quantities. These soaps can be made from Twitchell fatty acids, and large quantities are now being so made, the glycerine being previously removed and saved. As glycerine has no apparent detergent qualities and as it sometimes comes out on the soap, to its detriment, the soap is really better without the glycerine than with it, aside from the great money-saving.

Although many persons claimed that the glycerine made some difference in the appearance of the soap, it has been demonstrated to the satisfaction of a great many soap men, including the writer, that this is not so. The writer remembers one instance in particular where four soaps were prepared, one without glycerine and the other three with 5, 10 and 15 per cent. of glycerine respectively, and it was impossible to tell them apart by appearance, feeling or trial washing.

Also in the case of soft soaps there is no other way of saving the glycerine than by making them of fatty acids. Large quantities of soft soaps have been made in Europe by the Twitchell process for several years past. There has been ample demonstration, both in this country and Europe, that the removal of the glycerine from soft soaps makes no apparent change in the appearance or other properties of these soaps, nor in the washing properties. In fact it requires a careful chemical analysis to distinguish between the soaps with glycerine and those without. While some soft soaps are being made by the Twitchell process in this country, the matter has not been taken up in this respect to the extent that it should be, although it looks as if there would be an advance in this respect in the near future, especially since the price of glycerine has become so high.

Finally, this process is rapidly increasing in use in this country, Europe and in other parts of the world, and there is no doubt but what the next few years will see the process in such general use as to be almost universal.

[Contribution from the Laboratory of Arthur D. Little.]

HYGIENIC SIGNIFICANCE OF SULPHUR IN GAS.

By F E. Gallagher.

Received July 17, 1909.

Several states—namely, Connecticut, District of Columbia, Massachusetts, Wisconsin, and New York—have statutory limitations relating to the purity of illuminating gas, particularly in regard to sulphur. In addition to the state restrictions, there are local restrictions in a number of cities. In general these restrictions specify that the sulphur compounds shall not exceed 20 to 30 grains per 100 cu. ft. These laws can all be traced to arbitrary English legislation, and cannot be said to be based upon a rational experimental foundation.

Sulphur exists in illuminating gas mainly as carbon bisulphide, which upon burning goes to sulphur dioxide. Sulphuric acid may be formed under certain conditions by subsequent oxidation.

The experiments here described were made near a gas works (Malden, Mass.) from which gases containing different amounts of sulphur were obtained. A small room of 600 cu. ft. capacity was fitted up as a gas-burning room, and equipped with a fan for stirring the air and an exhaust fan for controlling the ventilation. Air samples were drawn from the room through Emmeling absorption towers containing hydrogen peroxide solution, which served to oxidize and absorb the sulphur dioxide, which was finally determined as $BaSO_4$. All results were corrected to standard pressure and temperature. There were determined in each experiment:

1. The amount of sulphur entering the room.
2. The sulphur dioxide content present in the air of the room.
3. Humidity.
4. Carbon dioxide content in the air of the room. This was used as a measure of the ventilation.

The ventilation was considered to be good when CO_2 equaled 6 to 12 parts per 10,000 and very restricted and unfavorable when CO_2 equaled 30 to 40 parts per 10,000.

Each individual experiment was run for 6 to 8 hours. Gas was always burned at the rate of 5 cu. ft. per hour.

The following are illustrative of the experiments made:

Expt. 1.—With one man in the room the ventilation was regulated so that the CO_2 equaled 7 parts per 10,000. The gas was then lighted and the average increase in SO_2 over several hours determined. With the sulphur in gas equal to 21.6 grains per 100 cu. ft., the average SO_2 content in the air equaled 0.28 part per million. With the sulphur in gas equal to 27.5 grains per 100 cu. ft., the average SO_2 content of air equaled 0.34 part per million.

Expt. 2.—The exhaust was regulated so that good ventilation was maintained with the gas continuously burning. With 18.6 grains gas, the SO_2 in the air under equilibrium conditions equaled 0.28 parts per million. With 31.6 grains gas, the SO_2 in the air equaled 0.49 part per million.

Expt. 3.—The ventilation was checked as much as possible, window and door closed and sealed, and exhaust fan stopped. The CO_2 content then equaled 38 parts per 10,000. With 23.3 grains gas the SO_2 value under equilibrium conditions equaled 0.53 part per million. With 35.8 grains gas the SO_2 value under equilibrium conditions equaled 0.77 part per million.

These experiments are but a few of many made. They illustrate, however, the general experimental scheme and indicate the extreme values encountered for SO_2 content in gas-lighted rooms; namely, 0.2 to 0.8 part per million. For conditions of good ventilation and with practically any commercial gas the limiting concentrations for sulphur dioxide in the air of rooms would be 0.1 to 0.4 part per million. For conditions of very restricted ventilation these limits would be 0.4 to 0.8 part per million.

As a result of extensive experiments, Lehmann showed that SO_2 in the air could not be detected below 6 parts per million; between 6 and 11 parts per million it would be just noticeable, while 14 to 20 parts would be somewhat disagreeable for people not accustomed to sulphur dioxide. He furthermore established[1] the fact that sulphur dioxide, when present in the air in such amounts as to be irritating to the nasal passages, produced no lasting physiological injury. In connection with this data our experimental results indicate that the SO_2 content of gas-lighted rooms is wholly negligible as regards comfort or health.

[1] K. B Lehmann: *Arch für Hygiene*, **18**, 180 (1893).

Further experiments bearing upon this problem gave the following results:

1. In no case, even under the most restricted conditions of ventilation, did the burning of gas give rise to noticeable odors of sulphur gases.

2. With the doors and windows sealed and the ventilation restricted as much as possible, the air of the room changed 1.8 times per hour. When the ventilation was rendered favorable for regular living conditions, the rate of change of air was several times greater than the figure just given.

3. As regards the vitiation of air by carbon dioxide, it was found that one man actively exercising had about the same effect as gas burning at the rate of 5 ft. per hour.

4. Paper on the walls and ceiling only moderately reduced the effectiveness of the plaster in the absorption of sulphur gases.

5. Sulphur gases formed on the combustion of illuminating gas are removed from the air of rooms in three ways: by the changing air in the ordinary course of ventilation, by condensation along with water vapors on the cold walls and windows, and through absorption by the alkaline constituents of the walls and ceilings.

6. As the sulphur content of a room increases markedly, the rate of reaction between the plaster and the sulphur gases becomes greater, thereby effecting a proportionally more rapid removal of the sulphur gases.

7. Calculations of the sulphur dioxide content of the air of rooms from the sulphur introduced by the inflowing gas are wholly unreliable if they fail to take account of the different ways in which sulphur dioxide escapes from a room.

The considerations and fears that originally prompted stringent sulphur-in-gas limitations were for the most part without justification and the liability of danger from sulphur has been greatly exaggerated and misunderstood.

MOISTURE DISCREPANCIES IN PHOSPHATE ROCK OF THE PACIFIC.

By Carlton C. James.

Received July 17, 1909.

The Committee on the Analysis of Phosphate Rock of the National Fertilizer Association presented a report some time ago which showed the results obtained by some thirty chemists upon

four samples of phosphate rock from the Southern States of South Carolina, Tennessee and Florida. These samples were prepared as uniformly as it was possible to make them, yet in the moisture determination the difference between the maxima and minima of the four samples ranged from 0.48 to 0.81 per cent. If the samples had been taken from the cars or cargo by thirty chemists individually in quantities that each thought sufficient, reduced to the form they considered proper, and in the way they deemed best, quartered and reduced by each in his own way to the desired size sample and placed in containers that each thought proper, it would not be unreasonable to suppose that the differences would show still more astonishing discrepancies. We have had occasion to study these differences in the phosphate of the Pacific with the idea of determining the causes and to reduce them as much as possible.

The material with which we have to deal comes from Ocean and Pleasant Islands, two small isles west of the Gilbert group and nearly on the equator. The material ranges in size from fine dust to rocks six inches in diameter. It is of coral origin and some of the larger pieces show distinctly the coral formation. Much of the material is in the form of spherical pieces resembling bird shot. Analysis of this material shows about 83 per cent. tricalcium phosphate, 3.5 per cent. to 4 per cent. calcium carbonate and usually less than 1 per cent. iron and aluminium oxides. This rock is received in cargoes of from 2000 to 4000 tons so that it is of considerable importance that representative samples be taken, not only for quality but for moisture as well. A difference of five- to eight-tenths per cent. in the moisture determinations would mean a financial consideration of $250 to $500, an amount about which probably no one would care to have any doubt as to whether it were his own or his neighbor's.

The sampling is done in a manner agreed upon by buyer and seller. As the rock comes out of the steamer practically one per cent. of the cargo is taken as sample: for a 2000-ton cargo the sample weighs about 25 tons. Every hundredth bucket- or basketful as it comes from the hold is set aside in closely woven sacks and held on board in a dry place until the cargo is discharged. The moisture sample is taken twice a day in glass jars holding at least two pounds. Usually Mason jars holding two quarts are used and any pieces too large to enter are broken with a hammer to a convenient size. When discharging is completed the moisture sample, weighing from 100 to 200 pounds, is combined in the presence of agents of buyer and seller and three samples of about five pounds each are taken. If there are many large rock pieces, these are again broken by hammer until they are about one-half to three-fourths of an inch in diameter. When both agents signify that they are satisfied the samples are sealed and each agent takes one for analysis; the third is retained for a referee in case the analyses should fall outside the limits set in the contract.

The quality sample of one per cent. of the cargo is sent in sealed bags to the fertilizer works where it is crushed and ground in the presence of the seller's agent to about 50 mesh. A small sample is taken from each 125 pounds. These are combined, quartered to about 25 pounds and three samples drawn as was done with the moisture sample.

The results of the analysis of several such samples are here given:

Moisture sample Per cent	Ground quality sample. Per cent.	Difference Per cent.
3.11	2.58	0.53
4.96	3.21	1.75
4.55	3.80	0.75
3.82	3.26	0.56
5.16	3.41	1.75

Each result given is the average of some six separate samples, all of which did not vary more than two-tenths per cent. It will be seen that the third column shows some remarkable differences between the moisture in the moisture sample and that in the ground sample.

By grinding the moisture sample in a small mill to about eight mesh it had been discovered some time ago that not only the size of the rock was reduced but the moisture content as well. Consequently, it was desirable that grinding and handling of the moisture sample should be practised as little as possible.

When the last above-mentioned result was obtained showing a difference of 1.75 per cent. between the two samples it was believed that a mistake had been made somewhere in the process of taking the sample or in its analysis, and suggestions were made that the jars in which the rock was placed were not entirely dry, that the drying temperature had been too high and that the samples had taken up moisture in cooling.

In order to shed some light upon the subject, during each day of discharging, tests were made

of the rock taken from the steamer and of the same rock from the mill after grinding. The results are as follows:

Unground. Per cent.	Ground to 50 mesh Per cent	Difference. Per cent.
3.72	3.48	0.24
3.75	3.58	0.17
3.51	3.34	0.17
4.01	3.88	0.13
3.43	3.16	0.27
4.58	4.28	0.30

The results given are averages of six determinations. Samples of 20 grams each were weighed into glass stoppered weighing bottles and dried in an air bath at 100° C. for five hours, both ground and unground samples being in the same air bath at the same time and cooled in the same desiccator so that the conditions should be as nearly identical as possible.

The results show that some moisture is lost in grinding but do not account for such a difference as 1.75 per cent. It had been noticed in weighing out the moisture sample that a representative sample depended to a considerable extent upon the operator. In a sample consisting mostly of fine and shotty particles there were embedded small pieces of rock from one to two and occasionally three centimeters in diameter. If the sample were shaken the fine particles would sift to the bottom and the larger particles would come to the surface, a point which had to be guarded against. Therefore, it was decided to make other experiments to determine if the size of the rock particles would have sufficient influence to make such a difference.

Three samples of 20 grams each were weighed into weighing bottles, duplicates being run at the same time. The samples were neither crushed nor ground and were subjected to no treatment other than that they were separated on screens according to size.

The first sample consisted of large rock pieces 15 mm. in diameter; the second, small pebbles 2 to 5 mm. in diameter; the third, fine particles through a 30-mesh screen. The samples were all placed in the same air bath and subjected to a temperature of 100–105° C. to constant weight which took about five or six hours. When all the samples showed constant weight, that weight was taken as the loss at 100–105° C. The temperature was then raised to 120–125° C. and was maintained thereat until constant weight was again established. Results:

	Diam. in mm.	Per cent. loss at 100–105°.	Per cent. loss at 120–125°.	Per cent loss between 100 and 125° C.
Rock pieces	15	3.361	3.519	0.158
Small pebbles	2–5	3.970	4.205	0.235
Through 30 mesh	0–0.8	4.858	5.062	0.204
Difference in loss between rock pieces and fine particles...	....	1.497	1.543	...

The loss at 120–125° C. is shown to be greater than that at 100–105° C. by about 0.2 per cent., but this may or may not represent water. In the case under consideration the loss may be due to organic matter: roots and stems which have become too small to be removed. Probably such a high temperature would never be used for obtaining the moisture in phosphate rock, and discrepancies due to this cause would be nil. The results also show that moisture is retained unequally in the sample and varies with the size of the particles. This no doubt is due to the greater surface exposed by the finer material, but whether the moisture varies in proportion with the fineness has not been determined. It is desirable to get a representative sample containing proportional parts of the fine and coarse material so that the correct amount of water may be determined, but as has been pointed out above, two difficulties are presented. If the sample is to be ground to particles of about the same size it would have to be reduced to 40 or 50 mesh with a loss of moisture, whereas, if it is left unground there must be left to the discretion and integrity of the chemist the procuring of correct results.

Other conditions and other material might not give rise to such discrepancies: we simply present these two points as they have occurred here, but from the results obtained here and those published by the National Fertilizer Association it would seem that the determination of water is not as simple as at first might be supposed and deserves more consideration than is usually given it.

Laboratory of the Pacific
Guano & Fertilizer Co.,
Honolulu, Hawaii.

[Contribution from the Laboratory of Arthur D. Little, Inc.]

THE ANALYSIS OF LEAD ARSENATE FOR WATER-SOLUBLE IMPURITIES.

By Roger C. Griffin

Received July 17, 1909.

Where large lots of any material are being held pending the result of the analysis of the sample, time becomes an important factor. The determina-

tion of water-soluble impurities in arsenate of lead according to the method of Haywood[1] requires at least eleven days and generally twelve. Our experience in the analysis of a considerable number of samples of this substance has led us to believe that the necessary time can be very materially shortened without sacrificing accuracy of results. In the first place, to determine whether it is necessary to shake the dried sample with water for as long a period as ten days, the following experiment was carried out:

Portions of two grams of the dried sample were weighed into large glass-stoppered bottles containing two liters of distilled water free from CO_2. Each bottle was thoroughly shaken about eight times each day. At the end of two days the contents of the first bottle (A) were filtered through a dry filter, 200 cc. of the filtrate evaporated to dryness in a weighed platinum dish on the water bath and the total soluble impurities dried at 100° in an oven for two hours, then cooled in a desiccator and weighed. At intervals of about two days the contents of one of the remaining bottles were treated in exactly the same manner, the contents of the last bottle being analyzed on the tenth day. The results obtained were as follows:

Bottle.	A.	B.	C.	D.
Days	2	4	6	10
Wt. of sol. matter (gram)	0.0075	0.0060	0.0065	0.0064
Per cent. of sol. matter (dry basis)	3.75	3.00	3.25	3.20

The increase after four days is seen to be insignificant since it is hardly possible to weigh closer than to 0.0005 gram under these conditions. On this account it also seems advisable to take 500 cc. for evaporation instead of 200 cc. On another sample tests were made after shaking for three days and for ten days, respectively, evaporating 500 cc. of the filtrate. The results were as follows:

Bottle	F.	G.
Days	3	10
Wt of sol matter (gram)	0.0253	0.0250
Per cent. of sol. matter (dry basis)	5.08	5.00

The difference between the results obtained from three days' shaking with water and those obtained from ten days' shaking is well within the limits of experimental error.

Considerable difficulty was often experienced in obtaining a clear filtrate, and the precipitate has considerable tendency to clog the pores of the filter paper and make the filtration proceed very slowly. We found, however, that with a Gooch crucible a perfectly clear filtrate could be obtained, and at the rate of 500 cc. in from 5 to 15 minutes. The asbestos mat must be thoroughly washed, of course, to remove any soluble matter or loose shreds. The filtration is also more rapid if the crucible and mat are ignited before use. The method of procedure which we finally found to be the most satisfactory and rapid is as follows:

The mat should be thick enough so that when held up to the light the holes in the crucible are not quite visible. After it has been prepared in the usual manner about 250 cc. of distilled water are poured through the crucible, followed by 5 cc. concentrated HCl and this in turn by 250 cc. more of water. The crucible is then strongly ignited for two or three minutes. After it is cool, 5 cc. of concentrated HCl are drawn through it and then 200 cc. of water. The suction flask is thoroughly rinsed out with water and as much as possible poured out. It is not necessary to dry either the flask or the crucible. About 25 cc. of the liquid to be filtered are sucked through the crucible, and the flask is rinsed out with this liquid and emptied. This is repeated twice and then the filtration is proceeded with until about 600 cc. of filtrate have been obtained. This is then poured into a graduated 500 cc. flask, after rinsing out the latter several times with small portions of the liquid, and made up to the mark.

After having weighed the total soluble matter, time may be saved by using this material for the determination of water-soluble As_2O_5. (It may be said here that in only two of the samples we have analyzed have we found any water-soluble PbO, one of these contained only a trace and the other 0.30 per cent. In case soluble PbO is present, however, it is necessary to evaporate another portion of the water extract for its determination.) The residue is taken up in a little water and evaporated with a few cc. of HNO_3. If it is evaporated directly with H_2SO_4, according to the method of Haywood, the H_2SO_4 chars the acetates which are always present (unless the arsenate was made from $Pb(NO_3)_2$) and the separated carbon causes considerable inconvenience. Evaporation to dryness with HNO_3 destroys these acetates. This dry residue is then taken up with a very little water and after adding 0.5 cc. of concentrated H_2SO_4, evaporated to a syrup on the steam bath, and then on the hot plate to fumes, to remove the HNO_3. From this point the method of Haywood as given in *Bulletin* **105** is followed.

[1] *Dept. of Agriculture. Bureau of Chemistry. Bull* **105**.

Briefly then, the method for the determination of water-soluble impurities in arsenate of lead, which we have found to give satisfactory results with a minimum expenditure of time, is as follows:

Two grams of the dried material are weighed into a large glass stoppered bottle containing 2000 cc. of distilled CO_2-free water, and allowed to stand three days, shaking frequently. The solution is then filtered through a Gooch crucible and 500 cc. of the filtrate are evaporated to dryness on the steam bath in a weighed platinum dish, dried to constant weight (two hours) in a water oven and weighed for total soluble matter. The latter is taken up with very little water and a few cc. of HNO_3, evaporated to dryness on the steam bath, washed into a small beaker with a little water and after adding 0.5 cc. of concentrated H_2SO_4 evaporated to a syrup on the steam bath and then to fumes on the hot plate. 10 cc. of water are added and the beaker gently swirled to throw any $PbSO_4$ into the centre. If any is present it is filtered out through a tiny filter paper, washing with 5 per cent. H_2SO_4. The As_2O_5 is determined in the filtrate according to the method of Haywood. If soluble PbO is present it is determined in a separate portion of the original filtered water extract by Haywood's method. The complete analysis can easily be carried out in five days.

The samples of arsenate of lead which have come under our observation have been very variable in composition. The total PbO has ranged from 64.32 per cent. to 73.28 per cent.; total As_2O_5 from 32.48 per cent. to 23.73 per cent.; total water-soluble matter from 1.96 per cent. to 5.08 per cent.; and soluble As_2O_5 from 0.12 per cent. to 1.95 per cent. These percentages are based on the dry material. The moisture in the original paste has varied from 43 per cent. to 68 per cent.

Haywood[1] gives the soluble As_2O_5 obtained from C. P. arsenate of lead as 0.63 per cent. to 0.85 per cent.

The water-soluble As_2O_5 in the commercial samples of lead arsenate has two possible sources: (1) dissolved arsenate of lead, and (2) disodium arsenate incompletely washed out of the material. The fact, however, that a sample may contain as little as 0.12 per cent. of water-soluble As_2O_5, whereas chemically pure lead arsenate has been found to dissolve sufficiently in water to give 0.85 per cent. of water-soluble As_2O_5, seems to indicate that lead arsenate is practically insoluble in water which contains even a very small amount of disodium arsenate. 0.12 per cent. of water-soluble As_2O_5 corresponds to 0.0019 gram of Na_2HAsO_4 per liter of water, or only about 2 parts per million. The water-soluble As_2O_5 in commercial lead arsenate therefore is due to the Na_2HAsO_4 present as impurity; and as this substance is comparatively easily soluble in water, it must all be dissolved out of 2 grams of lead arsenate by 2 liters of water in much less time than ten days.

[1] *Loc cit.*, p. 168.

ON THE VOLUMETRIC ESTIMATION OF URANIUM AND VANADIUM.

By Edward De Mille Campbell and Chas. E. Griffin.

Received June 16, 1909.

Up to this time there have been three volumetric methods proposed for the quantitative estimation of uranium and vanadium when occurring together. These methods have all been put forth because of the need for a rapid and accurate method for the analysis of carnotite ores.

The first of these is that of Friedel and Cumenge.[1] In this method the ore is dissolved in nitric acid and the vanadium, iron and aluminum are rendered insoluble by evaporating to complete dryness. Uranium and the alkalies are extracted by water containing a little ammonium nitrate. The vanadium, in acid solution, is reduced with sulphur dioxide and the uranium with zinc and sulphuric acid, after which each is titrated with standard permanganate.

A second method is that of A. N. Finn.[2] The ore is dissolved in dilute sulphuric acid (1 : 5), evaporated to fumes, cooled and diluted, An excess of sodium carbonate is added, the solution boiled and filtered and the precipitate washed with hot water. The precipitate is redissolved in the smallest possible amount of sulphuric acid and reprecipitated with an excess of sodium carbonate in order to insure complete extraction of the uranium and vanadium. The combined filtrates and wash waters are slightly acidified with sulphuric acid, 0.5 g. of ammonium phosphate added and the uranium precipitated as phosphate by rendering the solution alkaline with ammonia. The solution is filtered and the uranium estimated by dissolving the precipitate in sulphuric acid and reducing with zinc. The filtrate from the uranium phosphate is acidified with sulphuric acid, the vanadium re-

[1] *Amer. Jour. Sci.*, **10**, 135 (1900).

[2] *Jour. Amer. Chem. Soc.*, Oct., 1906.

duced with sulphur dioxide, and titrated, like the uranium, with a standard solution of potassium permanganate.

A third method is that of Fritchle.[1] The ore is dissolved in nitric acid, diluted with water, sodium carbonate added in excess followed by a large excess of sodium hydroxide. The sodium hydroxide retains the vanadium in solution but leaves the iron and uranium undissolved. This precipitate, after washing, is dissolved in hot, dilute nitric acid and the iron precipitated with ammonium hydroxide, the uranium being kept in solution by the addition of a large excess of ammonium carbonate. The uranium is reduced with strip aluminum and titrated with permanganate. The precipitate of ferric hydroxide is dissolved in dilute sulphuric acid, the iron reduced with aluminum and determined with permanganate. In a separate sample the uranium, vanadium and iron are reduced together with sheet aluminum and titrated with permanganate, the vanadium being calculated from the total amount of permanganate less that required for the uranium and iron. The assumption is made that the amount of permanganate required to oxidize vanadium reduced by sheet aluminum is approximately twice that which would be required if the vanadium had been reduced with sulphur dioxide.

The object of the present research was to devise a volumetric method for the determination of uranium and vanadium in the presence of each other, the method not involving a gravimetric separation of these two elements.

G. Edgar has proposed a method for the differential reduction of iron and vanadium[2] and another for the differential reduction of molybdenum and vanadium.[3] The iron is reduced to the ferrous condition and the vanadium to the V_2O_2 condition by the use of zinc and sulphuric acid in a Jones reductor. The reduced solution is caught in a titration flask containing a ferric salt. The solution of highly reduced vanadium reduces the ferric iron to the ferrous condition and the amount of reduced iron present registers the reduction of the vanadium. The solution is then titrated as if a solution of ferrous iron alone were to be reoxidized with permanganate.

The reduction of a vanadium solution to the condition of V_2O_2 and oxidation in the ordinary way with permanganate always fails to give accurate results for the reason that the solution of vanadium in this reduced condition has such a strong affinity for oxygen that it becomes partially reoxidized before the solution can be titrated. The use of the ferric alum as suggested by Edgar prevents this oxidation.

In the experiments tried in this laboratory slightly acid solutions of pure vanadyl sulphate and pure uranyl sulphate were used. The uranium solution was standardized by the usual method of precipitation and weighing as U_3O_8; also volumetrically by reduction with zinc and sulphuric acid and titration with standard twentieth-normal permanganate. The vanadium solution was standardized by reduction with sulphur dioxide, the excess of which was removed by the passage of a current of carbon dioxide through the boiling solution, followed by titration with permanganate.

Preliminary experiments were made to demonstrate that sulphur dioxide has no reducing action on uranyl solutions and that the titration of vanadium solutions when reduced with zinc and sulphuric acid to the V_2O_2 condition always requires less than three times the number of cubic centimeters of permanganate necessary to reoxidize when reduced with sulphur dioxide. Numerous experiments were made to determine the best conditions for the reduction and titration of uranium solutions.

Belouhoubeck in 1867 proposed the method for the reduction of uranyl solutions by zinc and sulphuric acid and titration with permanganate. Investigators since that time are much divided in opinion concerning the accuracy of results thus obtained. Some claim that the reduction proceeds further than the UO_2 stage and that the reduced solution needs exposure to the air in order to reoxidize to the UO_2 condition before the titration with permanganate is made. Among those supporting this view are Pullman,[1] Goettsch,[2] and McCoy and Bunzel.[3] Kern made extensive researches on uranium in 1900[4] and shows that the reduction does not proceed below the UO_2 stage when sulphuric acid is used, even upon five hours' boiling. All of the above used not less than fifty grams of zinc, and the ratio of concentrated acid to water varied from 1 : 6 to 1 : 4.

Kern used sodium carbonate in the titration

[1] *Eng. and Min. Jour.*, **70**, 548 (1900).
[2] *Amer. Jour. Sci.*, **26**, 79 (1908).
[3] *Ibid.*, **25**, 332 (1908).

[1] *Amer. Jour. Sci.*, **16**, 229 (1903).
[2] *Jour. Amer. Chem. Soc.*, **28**, 1541 (1906).
[3] *Ibid.*, **31**, 367 (1909).
[4] *Ibid.*, **23**, 685 (1901).

flask to create an atmosphere of CO_2 in order to prevent the oxidation of the uranous solution by air, but Pullman is of the opinion that this means was ineffective and that the reduced solution was really reoxidized to the UO_2 condition before the titration was made.

In numerous reductions which were made in this laboratory as Kern directs, except that not more than 15 grams of granulated zinc were used in any one reduction, it was found that results were not very concordant. It was thought that less violent reducing conditions would more easily effect the reduction of uranyl compounds in solutions not so strongly acid.

Reductions were tried on several solutions of uranyl sulphate containing 0.1023 g. of elemental uranium, gravimetrically standardized. In some cases 5 g. of zinc were used with 5 cc. of concentrated sulphuric acid and 95 cc. of water. The reduction was carried on at a slow-boiling temperature in an Erlenmeyer flask, the mouth of which was closed with a cork through which a small funnel passed. In some cases 2 cc. of free acid were added to 95 cc. of water, and in other cases one cubic centimeter was sufficient to effect the reduction. About 5 cc. of concentrated sulphuric acid were added when the reduction was thought to be complete; the solution was cooled somewhat and was then rapidly filtered through glass wool to remove undissolved zinc. After dilution to 150 to 175 cc. the solution was titrated with twentieth-normal permanganate. Results obtained in this way showed but small variation among themselves. The average of a large number gave a uranium content of 0.1036 g., or a positive error of 0.0013 g. from gravimetric results. The average of a large number of reductions carried on exactly in the way that Kern directs gave a larger positive error than this. Kern states that at least 45 minutes are needed for the reduction of 0.1 g. of uranium solution, but the reduction in the presence of relatively small amounts of free acid was always complete in a half hour, and more often in 15 minutes on this quantity of uranium, 0.2 g. was easily reduced in this manner in 45 minutes. The conclusion is that a solution more nearly neutral is more desirable for the reason that it is more rapid and the results show less variation among themselves. Pullman and others speak of the appearance of brownish colors when the reduction is effected with such large quantities of zinc and acid. This indicates reduction below the UO_2 condition. Working in the presence of relatively small amounts of free acid such color changes have not been noticed, and this may account for the uniformity in results obtained here, since there is no necessity for the reoxidation by atmospheric oxygen to the UO_2 stage.

Numerous experiments were made with other elements than zinc as reducing agents on mixed uranyl and vanadyl solutions. Among those tried were silver, lead, copper, and aluminum. Kern used aluminum[1] as a reducing agent for uranium and Fritchle used it for both uranium and vanadium. Silver, lead and copper offered no advantages which would suggest their use for this purpose. It was thought that some agent might be found which would reduce uranium to the UO_2 condition but at the same time would reduce the vanadium only to the V_2O_4 or V_2O_3 condition. The solution could then be tritated with permanganate in the ordinary way. Since uranium is more difficult to reduce than iron, and since vanadium is much more easily reduced than iron, any agent tried which completely reduced the uranium was found to reduce the vanadium to such a low state of oxidation that reoxidation by the air took place before the solution could be titrated. It was thought that possibly the oxygen of the air could be utilized in oxidizing the reduced solution to some definite point before titration with permanganate. Experiments were made to test the effect of bubbling air through the reduced solutions but it was found that conditions of acidity, concentration and temperature of the solution so influenced the results as to make them unreliable as a basis for a quantitative method.

Aluminum offered some advantages over zinc as a reducing agent for the reason that it left no residue in the solution and after reduction is completed the aluminum can be washed free of all adhering liquid very easily. It was effective in the reduction of both uranyl and vanadyl solutions. When strip aluminum was used in an open vessel with mixed solutions of these two elements, 2 or 3 cc. of sulphuric acid being present, reduction proceeded rather slowly. To hasten this process a spiral of heavy aluminum wire, wound to fit a ten-inch test-tube, was used. A mixed solution of uranyl sulphate and vanadyl sulphate was placed in the test tube and 50 cc. of water and 5 cc. concentrated sulphuric acid were added. The spiral was dropped in, the solution heated to

[1] *Jour. Amer. Chem. Soc.*, **23**, 685 (1901).

boiling over the naked flame and then immersed in a bath of boiling water. The tube was covered with a watch-glass. Reduction began at once and about five minutes after the lavender color characteristic of V_2O_2 had appeared the reduction was found to be complete. The test-tube and contents were cooled somewhat by immersion in running water, then the spiral was withdrawn by means of an aluminum hook fastened to a glass rod. A cubic centimeter or two of concentrated sulphuric acid was added and titration made with permanganate.

Using this manipulation with uranium solutions alone, the following results were obtained:

10 cc. uranyl sulphate solution required the following number of cc. of twentieth-normal permanganate:

11.54
11.34
11.34
11.40

15 cc. uranyl sulphate required

16.71
17.01

The calculated number of cubic centimeters of permanganate needed for 15 cc. of the above solution was 17.08. This figure was calculated from gravimetric results, weighing as U_3O_8 and assuming oxidation to take place on titration from UO_2 to UO_3.

When vanadium solutions alone were reduced and titrated in the same way less permanganate than the calculated amount was always needed, and this was the case with mixed solutions of uranium and vanadium.

As the vanadium content was lessened in proportion to the uranium content the results came nearer the calculated amount and became more uniform. This would be expected on account of the strong tendency of V_2O_2 to reoxidize in contact with air. To prevent this reoxidation 50 cc. of a solution of ferric alum, made by dissolving 26 grams of the crystallized salt in a liter of water slightly acidulated with sulphuric acid, were used.

The manipulation was as follows: The mixed solutions of uranium and vanadium were placed in a ten-inch test tube, 2 to 5 cc. of concentrated sulphuric acid added with 50 cc. of water, the tube heated on the open flame to boiling, then covered with a watch-glass and immersed in a boiling water bath until reduction was complete as indicated by the lavender or grayish color of the solution. The tube is cooled in running water until hydrogen bubbles just cease to rise from the surface of the spiral, the spiral drawn to the top of the test-tube with the aluminum hook, 50 cc. of the cold ferric alum solution are poured over the spiral and allowed to mix with the reduced solution, the spiral is drawn out and the solution titrated with twentieth-normal permanganate in the test-tube until nearly finished; a little free sulphuric acid is added, if necessary, and the solution finished in an Erlenmeyer flask at a temperature of 80°.

Operating in this way the following results were obtained, using 5 cc. uranyl sulphate solution and 5 cc. vanadyl sulphate solution:

Cc. twentieth-normal permanganate.	
18 39	18.49
18 49	18.74
18.34	18.7
18.59	18.65
18.68	

The calculated amount of permanagnate needed is 18.6 cc. This calculation is based on the assumption that the vanadium is reduced to the V_2O_2 condition and requires three times as much permanganate as the same quantity reduced with sulphur dioxide, while the calculation for uranium is the same as in uranium alone above.

Satisfactory results were obtained in this way when the uranium and vanadium were present in equal quantities; when the vanadium is greatly in excess the tendency to reoxidize is harder to overcome and the results show more variation.

To apply this method to a carnotite ore the manipulation would be as follows:

0.3 to 0.5 g. of the ore is dissolved in an Erlenmeyer flask in 40 cc. of 1 : 5 sulphuric acid or a mixture of nitric and sulphuric acids, if desired, care being taken to expel all the nitric acid by evaporation. The solution is evaporated until the greater part of the acid is driven off. It is cooled, diluted, an excess of sodium carbonate added and, while boiling, hydrogen peroxide is added drop by drop until the color of the precipitated iron shows it to be in the ferric condition. The solution is filtered and the precipitate washed with hot water. The precipitate is dissolved in the smallest possible amount of 1 : 1 sulphuric acid, an excess of sodium carbonate added, after which it is boiled, filtered and washed. The combined filtrates and wash waters are acidified with sulphuric acid and an excess of the acid added amounting to 2 to 5 cc. of the concentrated acid. Sulphur dioxide is passed in and when the color

indicates that the vanadium is reduced the solution is boiled and a rapid current of carbon dioxide passed through the boiling solution to expel the last traces of the sulphur dioxide. The titration is made on the hot solution with permanganate of a strength not to exceed twentieth-normal. The iron precipitate can be dissolved and the iron estimated in the usual way if desired.

The volume at this point can not conveniently be more than 75 cc. if the reduction with the spiral is to be carried on in one tube.

If the ore is quite rich it is well to divide the solution here and carry the reduction on in two test-tubes. The two solutions may be combined by pouring into the Erlenmeyer flask near the end of the titration and the titration completed as if the reduction had been carried on in one tube. From this point on the procedure is the same as in the reduction of the mixtures of the pure salts described above. The number of cubic centimeters of standard permanganate used in the titration of the reduced solutions in the test-tube minus three times the number of cubic centimeters used in the titration after reduction with sulphur dioxide gives the number of cc. needed to reoxidize the uranium alone from UO_2 to UO_3.

Four samples of carnotite thus treated gave for uranium, 15.92, 15.66, 15.26, 15.46 per cent.; for vanadium, 8.47, 8.57, 8.44, 8.44 per cent.

Edgar used a Jones reductor filled with zinc in the differential reduction of iron and vanadium and of molybdenum and vanadium. In a number of experiments in this laboratory, where a zinc reductor was used for the reduction of the uranyl and vanadyl solutions, the results obtained were not so satisfactory as those obtained with the apparatus above described. If it be true that the uranium is reduced below the UO_2 state, as Pullman and others suggest, then to pass it into a solution of ferric alum at once would give too high results, as far as uranium alone is concerned, but since some provision of this kind is necessary to prevent the reoxidation of the highly reduced vanadium it appears that an error is likely to occur in one direction or the other whether the ferric alum be used or whether it be omitted.

The method above described furnishes a convenient means of separating uranium and vanadium without the necessity of gravimetrically separating these two elements and of determining each with a degree of accuracy fully equal to that which can be obtained by any of the methods heretofore published.

UNIVERSITY OF MICHIGAN.
ANN ARBOR, June 14, 1909.

ON THE INFLUENCE OF THE TEMPERATURE OF BURNING ON THE RATE OF HYDRATION OF MAGNESIUM OXIDE.

By EDWARD DE MILLE CAMPBELL.

Received July 1, 1909.

In 1885 a court-house in Kassel, Germany, was seriously injured by expansion of the cement used in its construction. An investigation of the cause of this expansion was made by a government commission, of which Rudolph Dykerhoff, Dr. Ing. h. c., was Chairman. The cement used in the construction of the court-house was found to contain from 18–20 per cent. magnesium oxide. This led to a series of experiments to determine the influence of magnesia on Portland cement, and particularly the maximum amount which could be present without causing dangerous expansion. After more than twenty years of experimental work in Germany, France, England and the United States, different investigators have failed to come to complete unanimity regarding the maximum allowable per cent. of magnesia in Portland cement.

In an article entitled "Some Conditions Influencing Constancy of Volume in Portland Cements"[1] which appeared in 1906, the author, in conjunction with A. H. White, gave the results of a series of experiments extending over a period of four years, which showed that the expansion of Portland cement caused by magnesia was due to the slow hydration of free magnesium oxide, and that combined magnesia is without effect so far as expansion is concerned. The fact that the amount of expansion caused by the presence of magnesia is due more to the form in which the magnesia exists than to the total amount present offers a simple explanation for the differences in opinion of different investigators concerning the maximum allowable per cent. The expansion bars made from neat Portland cement containing free magnesia show that when kept in water the bar containing 1 per cent. of free magnesia has ceased to expand at the end of three years, that with 2 per cent. at the end of six years, while those with 3 per cent. and 4 per cent. have apparently not ceased expanding after eight years' immersion.

[1] *J. Am. Chem. Soc.*, **28**, 1273, Oct., 1906.

For many years it has been well known that certain natural cements, which are burned at a comparatively low temperature, but which often contain as much as 28 per cent. of magnesia, will give mortar or concrete as constant in volume as that made with good Portland cement. At the same time such natural cements cannot be depended upon, as not infrequently concrete made from such material will slowly expand and occasionally completely disintegrate from excessive expansion. Since these natural cements, high in free magnesia and yet giving satisfactory results, are burned at a much lower temperature than Portland cements, it would seem natural to expect that since the expansion is due to the hydration of magnesium oxide there must be some close relation between the temperature of burning and the rate of hydration.

In a special publication by Rudolph Dykerhoff, Dr. Ing. h. c., entitled "Ueber die Wirkung der Magnesia in gebranntem Zement," published in 1908, the author summarizes the results of his own experiments extending over a period of more than twenty years, and assumes that magnesium oxide burned at a low temperature hydrates readily and completely when immersed in water, but shows that the same oxide, when burned in a wind furnace at a temperature such as is employed for sintering Portland cement, combined with only about 3.5 per cent. of water during each of two evaporations to dryness.

The object of the experiments here described was to determine the quantitative relation existing between the temperature at which magnesium oxide from magnesite was burned and the rate at which such magnesium oxide would combine with water at ordinary temperature to form the hydroxide. The magnesite used for the work had the following composition: Silica 1.24 per cent., alumina and ferric oxide 1.32 per cent., calcium oxide 1.94 per cent., magnesium oxide 44.40 per cent., loss on ignition 51.06 per cent., total 99.95 per cent. The composition of the burnt magnesite from such materials would be by calculation: silica 2.53 per cent., alumina and ferric oxide 2.70 per cent., calcium oxide 3.96 per cent., magnesium oxide 90.78 per cent. If there was no combination of magnesium oxide after dissociation of the carbonate with silica, alumina or ferric oxide, the amount of water required to completely hydrate the magnesia according to the equation

$$MgO + H_2O = Mg(OH)_2$$

would be 40.51 per cent. of the weight of the burnt magnesite. Under the same conditions, the amount of water which would be required to satisfy the equation

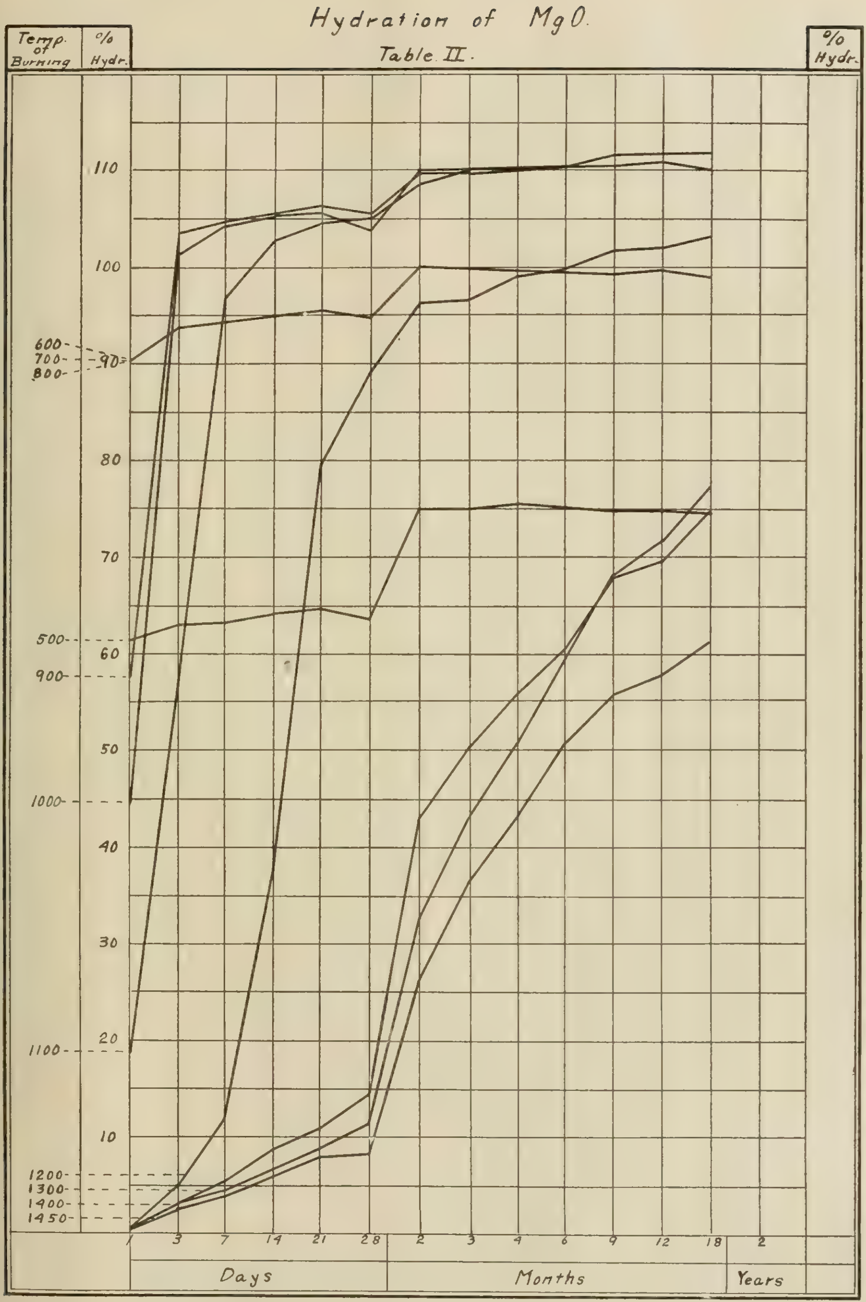
$$CaO + H_2O = Ca(OH)_2$$

would be 1.27 per cent. of the weight of the burnt magnesite.

In burning the various samples the method of procedure was substantially the same in all the cases. For temperatures up to 1000° C. 16–18 grams of the finely ground magnesite, contained in a magnesium oxide crucible, were placed in a Heraeus platinum resistance furnace. Two standardized platinum-rhodium thermocouples were used for measuring the temperature. One couple was placed in the annular space between the crucible and the side of the furnace, while the other was embedded in the center of the finely ground magnesite. The temperature of the furnace was gradually raised until the thermocouple inside the crucible containing the magnesite had reached the desired temperature, and after this had been reached the temperature was maintained for one hour. The furnace was then allowed to cool and the burnt magnesite removed, ground to pass a 100-mesh sieve, and quickly stoppered. For samples burned above 1000° C. the magnesite was first subjected to burning at a low red heat in order to completely remove carbonaceous matter and so prevent de-

TABLE I.

Length Hydr.	500°.	600	700°.	800°.	900°.	1000°.	1100°.	1200°.	1300°	1400°.	1450°.
1 day	24.83	36.61	36.51	36.52	23.40	18.00	7.61	0.43	0.46	0.58	0.34
3 days	25.45	37.63	37.92	38.65	41.00	41.93	22.84	2.05	1.25	1.24	0.93
7 days	25.64	37.93	38.30	38.51	42.26	42.38	39.22	4.85	2.17	1.85	1.55
14 days	25.89	38.21	38.55	38.72	42.59	42.73	41.65	15.28	3.32	2.74	2.43
21 days	26.09	38.38	38.69	38.89	42.75	43.06	42.34	32.23	4.43	3.56	3.29
28 days	25.48	38.03	38.45	38.64	42.05	42.73	42.13	36.15	5.75	4.11	3.35
2 months	30.58	40.63	40.61	40.41	44.46	44.39	43.97	38.92	17.36	13.24	10.64
3 months	30.51	40.38	40.47	40.33	44.51	44.57	44.69	39.12	20.29	17.55	14.81
4 months	30.66	40.38	40.47	40.29	44.58	44.57	44.69	40.02	22.55	20.48	17.55
6 months	30.59	40.35	40.45	40.29	44.64	44.70	44.86	40.48	24.54	24.12	20.45
9 months	30.39	40.35	40.39	39.94	44.72	44.85	45.18	41.19	27.48	27.60	22.59
12 months	30.34	40.34	40.53	40.32	44.88	44.92	45.33	41.34	28.99	28.12	23.31
18 months	29.99	40.03	40.14	40.03	44.63	44.54	45.34	41.74	31.22	30.31	24.85



Hydration of MgO.
Table II.
Temp. of Burning
% Hydr.
% Hydr.
110
100
90
80
70
60
50
40
30
20
10
600-
700-
800-
500-
900-
1000-
1100-
1200-
1300-
1400-
1450-
1
3
7
14
21
28
2
3
4
6
9
12
18
2
Days
Months
Years

terioration of the thermocouple embedded in the magnesite when a high temperature was reached. These samples were burned in a specially designed platinum resistance furnace which was capable of maintaining a temperature of 1450° C. for a good many hours without volatilization of the platinum and consequent burning out. The control of the temperature was such that in no case did the thermocouple inside the crucible containing the magnesite vary more than four degrees in the hour during which the material was being held at constant temperature.

Samples of one gram each of the burnt magnesite, ground to pass a 100-mesh sieve, were placed in a series of weighed porcelain crucibles. Sufficient distilled water was then placed in each crucible to completely cover the sample. As soon as the samples were covered the crucibles were placed in a vacuum desiccator containing concentrated sulphuric acid, and the water was allowed to evaporate. Samples which were covered with water one day and placed in a vacuum desiccator over sulphuric acid appeared dry the following day. The rack containing the set of crucibles was then placed in a drying-oven at from 102°–105° C. and allowed to remain over night. After cooling, the crucibles were weighed, and the gain in weight taken as the one-day hydration. After the one-day hydration water was again added, and the samples allowed to stand in a closed desiccator containing some water for two days, after which they were again dried *in vacuo* over sulphuric acid for one day, and again in a steam drying-oven over night. This second gain in weight was taken as the hydration after a total of three days. A similar method of hydrating and drying—first *in vacuo*, followed by steam drying-oven—was used for the hydrations up to and including the twenty-eight day test. Through an oversight the samples in this last case were left in the drying-oven two days before weighing. The fact that the samples dried in the drying-oven lost appreciably after prolonged drying led to a change in the method of drying after the twenty-eight day test. Beginning with the two-month test the samples, after allowing to stand covered with water at room temperature, were placed in a vacuum desiccator over sulphuric acid and allowed to remain until the weight had become practically constant. This usually required from seven to nine days. The percentage gain in weight of the various samples, after the different periods of hydration, is given in Table I.

The table shows clearly that at 500° C. the magnesite was not completely dissociated in one hour. Experiments made in this laboratory upon calcite showed very slight dissociation at 600° C. after an hour's heating. Since magnesium oxide alone probably exists as such in the sample burned at 600° C., and since such magnesium oxide, as stated in the earlier part of this paper, would require 40.51 per cent. of the weight of the burnt magnesite for complete hydration, this amount has been taken as the basis for computing the curves given in Table II, which shows graphically the progress of the hydration.

A study of the curves, considered in connection with the fact that samples after hydration lose some of their water when dried in a steam-oven, seems to indicate the following conclusions:

1. That magnesite is not completely dissociated at 500° C. in one hour under the conditions used in the experiments.

2. That dissociation of the magnesium carbonate is complete at 600°, while that of calcium carbonate is not.

3. That the hydration of magneisum oxide burned at 600°, 700° or 800° C. is practically complete in three days.

4. That between 800° and 900° C. the calcium carbonate is dissociated, and that combination takes place between basic and acidic oxides, resulting in the formation of silicates or aluminates. The silicates or aluminates so formed combined with more water than would be required for the complete hydration of the basic oxides alone.

5. That a change in the constitution of the magnesium oxide sets in between 1000° and 1100° C. resulting in a marked decrease in the rate of hydration, and that this change becomes more marked with rise of temperature of burning, until at 1450° C., or nearly the temperature required for burning Portland cement, the magnesium oxide after eighteen months' immersion in water has combined with only 61.4 per cent. of the water required for complete hydration.

Chemical Laboratory, University of Michigan, Ann Arbor.
June 18, 1909.

FREE LIME IN PORTLAND CEMENT. A MILL STUDY.

By Arthur G. Smith.

Received July 17, 1909.

The purpose of this paper is to present actual results obtained by testing for free lime both the night and day runs of portland cement as manu-

factured at the mill according to the microscopic method of detecting free lime, as published by Alfred H. White.[1]

A preliminary statement as to how samples are taken and observed is necessary here to properly interpret the results following. From four tube mills grinding finished cement a sample was taken each hour in the twenty-four, upon which tests for fineness, setting time and soundness were made. This gave a very accurate set of results showing the nature of the product leaving the mills for each hour. The pats so made from these separate samples, were, after 24 hours, kept in boiling water seven hours and a careful record made as to their condition. It will be noted that the results are reported as the number of perfect pats, number of fair pats and number of bad pats. By perfect pats are meant those which were strong, neither checked nor warped, and free from cracks; fair pats, those slightly checked or warped; bad pats, those badly checked, cracked or disintegrated. In addition to the hourly samples taken, a general average sample was taken on each shift. To get this sample as nearly an average of the output of all four mills as possible it was decided to take it from the screw conveyor carrying the cement to the stockhouse. The method devised is as follows: In the bottom of the screw conveyor housing a hole about 1/8 inch in diameter was bored and so placed that it was directly under the flight of the conveyor. From this it will be seen that upon each revolution of the screw a small portion of the cement was forced through the opening and collected. It was upon this general average sample from each twelve-hour run that the microscopic tests were made. The results covering a two-week run are herewith tabulated:

DAY RUN.

1909. Date.	Prediction from microscopic test of average sample.	Boiling test	General average.	Perfect.	Fair.	Bad.
June 3	Perfect (Trace)	Perfect Total pats......	47	45		2
" 4	Perfect (Trace)	Perfect Total pats......	48	41	4	3
" 5	Perfect (Trace)	Perfect Total pats......	48	45	1	2
" 6	Perfect (Trace)	Perfect Total pats......	48	47		1
" 7	Perfect 1/8 bad	Perfect Total pats......	48	39		9
" 8	Perfect (Trace)	Perfect Total pats......	46	44		2
" 9	Perfect (Trace)	Perfect Total pats......	46	44		2

[1] THIS JOURNAL, 1, 5, January, 1909.

DAY RUN (*Cont.*).

1909. Date.	Prediction from microscopic test of average sample.	Boiling test	General average	Perfect	Fair	Bad.
June 10	Perfect (Trace)	Perfect Total pats......	25	25		
" 11	Perfect About 1/6 bad	Perfect Total pats......	48	40	1	7
" 12	Perfect 1/4 bad	Perfect Total pats......	48	38		10
" 13	Perfect (Trace)	Perfect Total pats......	48	48		
" 14	Perfect (Trace)	Perfect Total pats......	48	48		
" 15	Perfect (Trace)	Perfect Total pats......	46	45		1
" 16	Perfect 1/4 bad	Perfect Total pats......	43	36	2	5

NIGHT RUN

1909. Date.	Prediction from microscopic test of average sample.	Boiling test	General average	Perfect	Fair	Bad.
June 3	Perfect About 1/4 bad	Perfect Total pats	44	35		9
" 4	Perfect About 1/4 bad	Perfect Total pats..	48	40	6	2
" 5	Perfect About 1/4 bad	Perfect Total pats ...	48	39	4	5
" 6	Perfect (Trace)	Perfect Total pats......	48	45	1	2
" 7	Perfect 1/3 bad	Perfect Total pats......	48	36	8	4
" 8	Perfect 1/4 bad	Perfect Total pats......	48	40	2	6
" 9	Perfect (Trace)	Perfect Total pats...	37	36		1
" 10	Perfect (Trace)	Perfect Total pats......	46	44		2
" 11	Perfect 1/3 bad	Perfect Total pats	48	32	5	11
" 12	Perfect (Trace)	Perfect Total pats	48	45		3
" 13	Perfect (Trace)	Perfect Total pats	48	48		
" 14	Perfect (Trace)	Perfect Total pats......	41	41		
" 15	Perfect 1/4 bad	Perfect Total pats.	38	32	4	2
" 16	Perfect 1/8 bad	Perfect Total pats......	43	37	3	3

In making our prediction with the microscope we endeavored to estimate the number of the hourly pats which we thought would be bad, judging from the amount of free lime present in the average sample. It will be noted that in most cases the prediction with the microscope checked very accurately with the boiling tests.

In predicting results by the microscopic method, we practically assumed that no other agencies besides free lime were causing unsoundness in the cement. We think we were justified in this, because the routine operation at this plant is very favorable for elimination of the other factors which might cause unsoundness except free lime, it being the standard practice to grind the raw materials, consisting of limestone and clay, to a fineness of

not less than 97 per cent. through a 100-mesh screen and the finished cement to an average fineness of 98 per cent. through a 100-mesh sceen and 83 per cent. through a 200-mesh screen. Further, the raw materials contain less than the average proportion of ingredients which might cause unsoundness.

It will be noted that on each shift there were some few hourly pats which did not perfectly pass the boiling test. We attribute this to two causes: first, an occasional non-uniform mix of the raw materials, and second, to the formation of "rings" in the kiln. It is the nature of the class of raw materials used to cause "ringing" in the kilns, and when these so-termed "rings" have to be barred out, some underburned clinker is very likely to go through the kiln. This underburned clinker has no chance to age as the clinker passes direct from the kilns through a cooler and is ground to finished cement in from six to eight hours after leaving the kilns.

CONCLUSION.

It is the writer's belief that the microscopic test for free lime will be a great aid to the manufacturer. If the results obtained can be made quantitative, and an accurate method for sampling devised, good results must be obtained.

COPPER-CLAD STEEL—A NEW METALLURGICAL PRODUCT.

By Wirt Tassin.

Received July 1, 1909.

For many years past attempts have been made to cover steel with a copper coat which could be of any desired thickness, and to so firmly weld the two metals that the combined product could be submitted to any of the usual methods for working metals without destroying the integrity of this weld.

The many methods tried in the past have been more or less successful failures, either from a metallurgical or a commercial standpoint, and it is only recently that a process has been developed for the successful welding of copper to steel in such a manner that it will stand the many methods used for working metals, and be at the same time a commercial metallurgical product. The weld between the copper and the steel is perfect within the limitations of a metallurgical process. The copper can be separated from the steel only by melting it off. The weld will resist sudden temperature changes such as heating the combined metals red hot and then quenching them in ice-water. It will resist both stress and shock. In the accompanying illustration (Fig. 2) a section of a round is shown that has had its copper cut through to the steel, the section placed in a vise and repeatedly struck with a hammer.

The process by which this result is obtained may be described as follows: Steel of any desired composition and shape, which, for the purpose of this description will be regarded as being a mild basic open-hearth steel, rolled into rounds and cut into 26″ billets, to make wire rods, is sand-blasted and pickled to remove scale. The billet, which has previously been drilled and tapped at each end, is hung by means of a rod and bushing screwed into one end, in a pre-heater and is brought to a red heat. When the desired temperature has been reached, the billet is then drawn into a tube (also previously heated) by means of a rod which is screwed into the top of the bushing. This rod slides up and down in the center hole of a three-jawed chuck, which holds the tube and centers the billet in it. A steel flange is then screwed on the bottom of the billet, thus forming with the tube a mold in which the billet is the core.

The mold and billet are now carried to a pot of specially prepared copper which is in a super-molten condition. The billet with its attached flange is now lowered out of the tube and into this copper, and kept there for a length of time sufficient to wet the surface of the steel and to form an alloy film. The billet is then drawn from the copper up into the tube, and the billet and its mold is carried to a second pot containing commercially pure copper, in which the final coat of copper is applied. The mold with its billet as a core is lowered into this pot and the molten copper rushes in through two openings in the top of the tube until the mold is filled. The mold is then withdrawn from the second crucible, and when the copper has frozen, the chuck, rod and flange are unscrewed. The tube and its contents are next placed in a ram and the copper-clad steel billet is pushed out of its mold. The billet is now given a washing heat and is then rolled to the desired size.

The rolling is, in general, similar to that of steel or copper, and it is interesting to note that in spite of the great differences between the physical properties of copper and steel, the two metals when so welded have, under proper conditions, practically the same rate of flow. The proportional areas

of the copper and the steel remains practically a constant from the larger to the smaller sizes.

The tensile strength of copper-clad is also remarkable. Regarding the metal as having 40 per cent. of its sectional area made up of copper, its tensile strength after the proper treatment is equal to, and may be greater than that of a steel having a composition similar to that of the steel in the copper-clad, but whose sectional area is equal to that of the clad metal. An illustration of this may be seen in the following table of commercial wires, in which due allowance must be made for the difference between hard and soft drawing:

Name.	Diam. in inches.	Breaking weight in lbs.
Galvanized steel	0.162	1406
B. B.	0.162	1250
E. B. B.	0.162	1140
Copper	0.162	1237
Copper-clad	0.162	1874

having a relatively low elastic limit, gives a figure directly comparable with that of a steel treated under like conditions whose sectional area is equal to that of copper-clad, and whose composition is similar to that of the steel composing its core.

Copper and steel in the presence of moisture form a galvanic couple, and the corrosion of the steel proceeds with great rapidity. The resistance to corrosion of copper-clad so far as the copper coating is concerned is, of course, the same as that of copper. But, in view of the marked galvanic action set up between copper and steel, it would be assumed that corrosion would quickly occur at the exposed ends, and be a constant factor so long as an electrolyte was present. This supposition is not so, at least in the presence of fresh or salt water. Test samples placed in water, through which a current of air has been allowed to bubble continuously for three months, demonstrated that after a certain period of time, somewhere between 15 and 40 days, corrosion practically ceases, as shown by taking the loss in weight of the tests at varying periods. It is believed that this stopping of corrosion is a result of the following conditions:

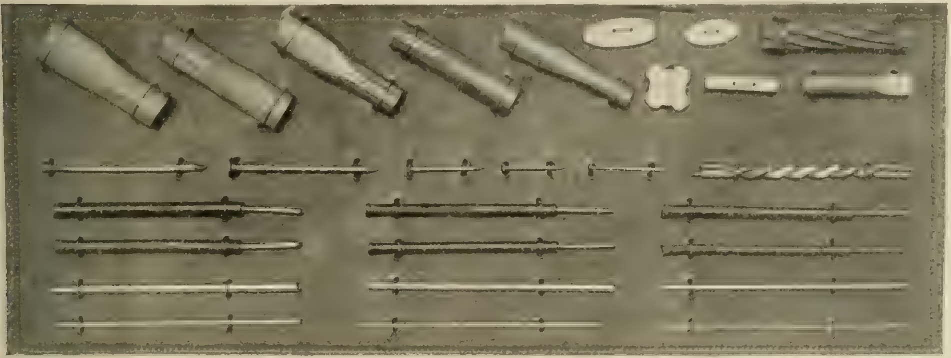


Fig. 1.

This table is an illustration of the fact that the tensile strength of copper-clad is not the mean of the strength of copper and steel, for the composition of the steel in the galvanized wire quoted is practically that of the steel in copper-clad, and, making liberal allowance for the difference in the heat treatment of the two, the breaking weight of the copper-clad is equal to, if not greater than, that of the galvanized, and but six-tenths of it is steel.

The above statement is also true of its elastic limit, which will average 90 per cent. of its tensile strength. The elastic limit of copper under the best conditions is 60 per cent. of its ultimate strength. That of steel is a variable, but for comparison take it at 90 per cent. Copper-clad steel, four-tenths of whose sectional area is a metal

After a certain amount of rust has been formed, it appears that a thin film of copper mixed with some copper oxide is plated out or deposited between the iron oxide and the unattacked steel, and that this film will act as a preservative coat as long as it remains intact. If broken, further oxidation sets up and the process simply repeats itself. While it is true that the corrosion on the end of a wire is not a factor in its life, yet the corrosion of the end of a relatively large diameter

may become very serious. If the above observations hold true on larger sizes (so far it has not been tried on sizes above 3/8"), it will have quite a bearing on material suitable for marine work. Tests along this line are now being carried out, and the evidence to date points to a confirmation of the observations made on the smaller sizes.

The uses to which copper-clad steel may be put are many. The first and most obvious is a wire to be used for electrical and mechanical purposes. The conductivity requirements for electrical use depends directly upon the amount and kind of copper used in the coat. Thus a copper-clad wire, four-tenths of whose sectional area is copper, will have a conductivity of 40, since both copper and steel wire possess certain disadvantages for electrical work: the one having a low tensile strength and under given conditions a lack of toughness, the other having a low conductivity and is subject to a more or less rapid corrosion. Copper-clad wire has a strength and toughness equal to that of steel, a conductivity far greater than that of steel, and it will not corrode. For example, in telephone work the life of a line is dependent upon its breaking weight and elastic limit. The breaking weight and elastic limit of a No. 10 copper wire are respectively 530 and 293 lbs., while that of a No. 14 copper-clad is 760 and 320 lbs. The one weighs 166 pounds per mile and the other 61. Comparing copper-clad with galvanized iron telephone wire, a much smaller size of copper-clad may be used for the same ohmic resistance, thus:

Wire.	Diam. in inches.	Ohms per mile at 68° F.	Weight per mile. Lbs.
E. B. B.	0.134	18.83	250
B. B.	0.134	22.04	250
Copper-clad	0.134	7.50	266

Where a high tensile strength and resistance to corrosion is an essential and an increased conductivity is desirable, as for example in power transmission requiring long spans and in catenaries, its value is apparent.

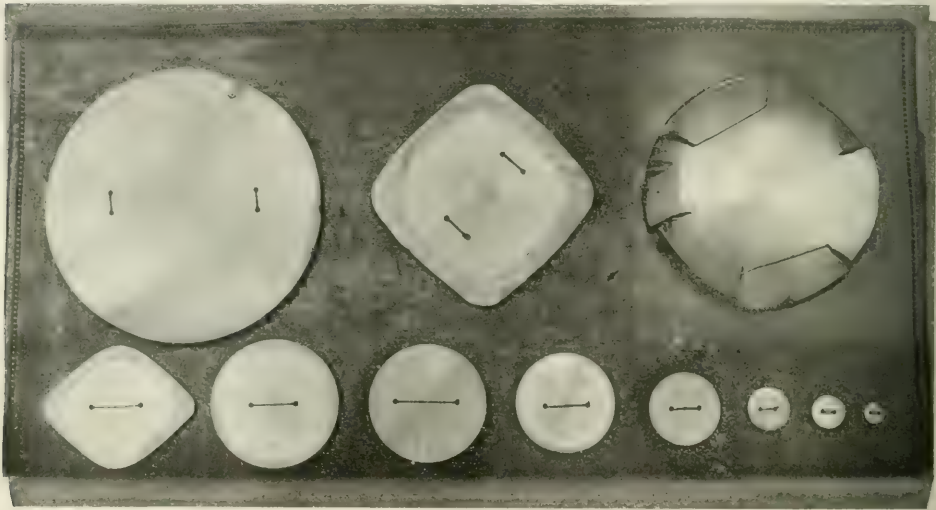


Fig. 2.

For mechanical purposes, such as bridge work, derrick guys, rigging, springs, rounds of all sizes suitable for anchor bolts, pump rods, etc., where resistance to corrosion combined with a high tensile strength is an essential, copper-clad is admirably adapted since steel having any desired physical qualities may be used as the core.

For large structural shapes it is questionable whether or not this material will ever have a commercial use, but for light shapes suitable for skylight and similar work, its value is obvious. It is non-corrodible and possesses the strength of steel. Copper is weak, galvanized iron corrodes.

To sum up, the material has a greater strength

than copper, and, under given conditions, is equal to, if not greater, than that of steel. It has a greater conductivity than steel and less than that of copper. Its resistance to corrosion is equal to that of copper and immeasurably greater than that of steel.

A SERIES OF PARALLEL DETERMINATIONS WITH THE MAHLER AND PARR CALORIMETERS.

By S. W. Park and W. F. Wheeler.

Received July 10, 1909.

The samples used in this series of parallel tests were kindly furnished by fuel engineering companies and inspection chemists in the course of regular inspection work from the larger commercial centers, such as New York, Pittsburg, Chicago, Birmingham, Louisville, Topeka, etc. An examination of the record shows the samples to have come from the following states: fourteen from Pennsylvania, eight from West Virginia, seven from Illinois, six from Kansas, three from Kentucky, two from Alabama, and one each from Maryland and Indiana.

It was sought also to cover a wide range in composition, and in consequence the ash constituent is seen to vary from three per cent. to twenty-two per cent. and the sulphur from one-half to five and one-half per cent.

For the bomb calorimeter the Mahler-Atwater type was employed, being platinum-lined and using oxygen from the Lindé Air Products Company. The bomb was standardized by means of pure naphthalene, using 9692 calories as the value of that substance. A Beckmann thermometer, graduated to hundredths of a degree, corrected by the Bureau of Standards at Washington, was used in both series of tests.

In the Parr calorimeter the procedure was simplified to the extent that all coals were air-dried to a content of moisture not exceeding 3 per cent. and, in consequence, no further drying in the oven was needed. In addition to the sodium peroxide, the uniform amount of one gram of pure potassium chlorate as accelerator was used in the charge, with the usual one-half gram sample of coal. The rise in temperature was corrected by a factor made up of the following components:

Each per cent. of ash was multiplied by	0.00275° C.
Each per cent of sulphur was multiplied by	0.005° C.
The correction for heat reaction of the accelerator was	0.130° C.
The heat of combustion for the fuse wire was	0.008° C.

This correction factor was uniform for all of the coals excepting those of the Illinois-Indiana type, which had an additional correction of 0.024° C. This additional factor is made necessary by reason of the high percentage of hydration or water of composition which characterizes the coals of this type. They are readily distinguished by the fact that their normal content of water is high, exceeding 5 per cent. Another characteristic is the high content of volatile matter which results in a low ratio of fixed carbon, the latter constituent being almost without exception below 50 per cent. of the coal. The deriving of the correction factors in this manner greatly simplifies this phase of the process, and as is evident from an examination of the table, it is applicable to all the wide variations, not only in type of coal, but in ash and sulphur content. In the table of results which follows, the variations ± are calculated to percentages of the Mahler values. It will be seen that the average variation of the entire forty-two coals is 0.03 per cent., the highest variation being 0.7 per cent. There are only three cases where this amount of variation occurs. The results are, therefore, in remarkably close agreement, indeed approximating the duplication of results that is ordinarily possible with good manipulation by means of the same instrument.

Attention should be called to the anthracites, Nos. 28 and 29. These have had a correction made for the unburned carbon. After dissolving the fusion and acidifying, the unburned material was caught upon a filter, dried and swept into a counterpoised capsule for weighing. Sample 28, for example, has as an average of three determinations, 2.82 per cent. of unburned carbon. The indicated heat value, therefore, applying the usual correction for ash, sulphur, etc., was 12775, and this multiplied by 1.0282, gave as a final value 13135 B. T. U. In sample No. 29 the indicated heat value was 12595 and the unburned coal was 2.867, hence the final value was 12595 × 1.0286 or 12955 B. T. U.

Concerning this additional correction, it may be well to note the necessity of making a similar correction for anthracites in using the bomb calorimeter. No determination on such material is reliable which does not take account of the unburned substance remaining in the bomb. This is especially notable in anthracites with an ash content above 6 or 7 per cent. For example, with the anthracite sample No. 28, the washings

from the bomb were filtered through a Gooch crucible, weighed and ignited as for an ash determination. The loss of weight was 0.010. This loss represents pure carbon, hence it should have added to it the proportionate amount of ash and moisture in order to bring the loss to the same basis as the initial coal for correcting the weight taken or actually burned. The combined weight of ash and moisture is 0.1241 gram, hence the above loss of 0.010 is divided by (1.00 — 0.1241) or 0.8759, giving 0.0115 as the amount of unburned coal. This figure, subtracted from the coal as weighed out, gives the amount of coal actually involved in the combustion and which must be used in calculating the Mahler value.

Occasionally coals of the bituminous type are met with, sufficiently high in carbonate of lime to require a correction for the Mahler process, due to the heat required to dissociate the $CaCO_3$. This amounts to 7.86 B. T. U. for each per cent. of calcium carbonate present and, as coals of the central-western type are not infrequent with four or five per cent. of this material present, it constitutes a variable that may properly receive attention where that type of apparatus is employed.

In the case of sample No. 45, use was made of this coal to test the effect of abnormally high ash upon the heat of fusion with sodium peroxide and thus verify the correction factor made use of for the ash. This is a bone coal and the correction factor amounts to a total of 0.270°. The results are in sufficiently close agreement to establish the correction factor as applicable to even such a high ash as is here shown. While the factors as herein made use of are slightly altered from those formerly published,[1] the variations are chiefly in the distribution of the correction factors. For ex-

THE PARR CALORIMETER IN COMPARISON WITH THE MAHLER-ATWATER BOMB.

Tab. No.	Lab. No.	Locality.	Moisture. Per cent.	Ash. Per cent.	Sulphur. Per cent.	Calories by Mahler-Atwater bomb.	Calories by Parr calorimeter.	Diff. in calories.	Diff. in per cent. of bomb value. Per cent
1	2090A	Williamson Co., Ill.	2.32	11.60	2.67	6922	6907	—15	—0.2
2	2111	Kanawha, W. Va.	0.88	10.70	1.82	7571	7587	+16	—0.2
3	2112	Pittsburg seam	1.07	10.41	1.26	7496	7527	+31	+0.4
4	2113	Kanawha splint	1.12	14.94	0.92	6982	6970	—12	—0.2
5	2114	Fox Ridge, E. Ky.	1.31	8.63	4.41	7559	7540	—19	—0.2
6	2115	Pittsburg seam	1.00	11.35	1.79	7446	7449	+3	0.0
7	2116	Waverly, W. Ky.	1.88	11.92	3.83	6926	6929	+3	0.0
8	2119	Frontenac, Kan.	1.16	12.14	4.80	7200	7159	—41	—0.6
9	2120	Frontenac, Kan.	1.79	8.08	3.20	7621	7618	—3	0.0
10	2121	Frontenac, Kan.	1.12	20.46	5.58	6405	6415	+10	+0.2
11	2122	Frontenac, Kan.	1.80	6.29	3.00	7786	7814	+28	+0.4
12	2123	Frontenac, Kan.	1.43	13.76	3.44	7066	7084	+18	+0.3
13	2124	Frontenac, Kan.	1.90	5.98	3.09	7783	7798	+15	+0.2
14	2125	Black Creek, Ala.	1.92	12.63	0.93	7434	7450	+16	+0.2
15	2126	Little Warrior, Ala.	0.88	15.53	0.82	7100	7153	+53	+0.7
16	2127	Pa. Gas, Wash. Co., Pa.	1.53	8.32	0.97	7624	7659	+35	+0.5
17	2128	George's Creek, Md.	0.78	8.51	1.12	7904	7895	—9	—0.1
18	2129	Somerset Co., Pa., Knickerbocker	0.79	9.10	0.96	7854	7826	—28	—0.4
19	2130	Somerset Co., Pa., Quemahonig	0.66	6.73	1.00	8088	8066	—22	—0.3
20	2131	Cambria Co., Pa., Henriette	0.79	4.89	0.72	8313	8291	—22	—0.2
21	2132	Cambria Co., Pa., Henriette	0.65	4.12	0.70	8406	8360	—46	—0.5
22	2132	Cambria Co., Pa., Naut Y Glo	0.64	6.16	1.41	8179	8148	—31	—0.4
23	2134	Cambria Co., Pa. Sterling	0.57	4.99	1.26	8285	8225	—60	—0.7
24	2135	Cambria Co., Pa., Pardee	0.89	7.53	1.63	7957	7991	+34	+0.4
25	2136	Cambria Co., Pa., Miller's Vein	0.73	4.59	0.52	8332	8313	—19	—0.2
26	2137	Cambria Co., Pa., Sugar Loaf	0.66	5.89	1.31	8163	8176	+13	+0.1
27	2138	Cambria Co., Pa., Sugar Loaf	0.51	6.06	2.64	8201	8148	—53	—0.6
28	2139	Anthracite	1.19	11.22	0.80	7284	7296	+12	+0.1
29	2140	Anthracite	1.04	13.13	1.20	7153	7197	+44	+0.6
30	2141	Pocahontas	0.73	5.05	0.64	8294	8241	—53	—0.6
31	2142	Pocahontas	0.91	16.51	1.25	7097	7109	+12	+0.2
32	2144	Floyd City	1.71	4.89	0.99	7808	7845	+37	+0.5
33	2180	Vermilion Co., Ill.	2.28	22.40	5.07	5931	5920	—11	—0.2
34	2193	Indiana Block	2.39	8.14	2.54	7278	7309	+31	+0.4
35	1003	O'Fallon, Illinois	2.31	12.64	4.79	6605	6652	+47	+0.7
36	1114	Saline Co., Illinois	2.55	8.81	2.41	7194	7200	+6	+0.1
37	1543	Pocahontas	0.85	3.23	0.71	8447	8425	—22	—0.3
38	1545	Williamson Co., Ill.	4.33	9.02	1.89	6966	6982	+16	+0.2
39	1763	Thayer, Ill.	2.90	10.66	4.82	6755	6789	+34	+0.5
40	1878	Murphysboro, Illinois	2.41	4.64	0.69	7631	7581	—50	—0.6
41	1884	Westmoreland, Pa.	1.18	5.29	0.98	7998	8029	+31	+0.4
42	1999	W. Va. gas coal	0.94	3.66	0.70	8051	8073	+22	+0.3
43	2000	Pocahontas	0.52	5.26	0.56	8288	8247	—41	—0.5
44	2005	Vermilion Co., Ill.	2.23	17.48	4.32	6412	6393	—19	—0.3
45	2392	Bone coal	6.02	38.71	5.85	7240	7194	—46	—0.6

[1] *Jour. Am. Chem. Soc.*, **29**, 1606.

ample, the hydration of the ash is found to require a larger factor for that constituent with a correspondingly smaller one for that form of hydration which has been designated as water of composition.

With any method of heat determination too much emphasis cannot be placed upon the need of care in manipulation. It must be remembered that small errors in reading and a disregard for radiation and thermometer corrections are multiplied by two or three thousand in the final results.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF MISSOURI.]

THE DETERMINATION OF PHOSPHORUS IN FLESH.

[FIRST PAPER.]

BY P. F. TROWBRIDGE.

Received July 6, 1909.

During the winter of 1907–8 the author attempted to prepare the ash from a number of samples of meats for a further study of the mineral constituents of flesh.

A large platinum dish was used and the ignition of the dry sample was made in a muffle furnace at a very low heat. The platinum was attacked within a very few minutes and the analysis of a piece of the fused bottom of the dish showed the presence of phosphorus. This raised the question whether or not phosphorus was being volatilized from the regular meat samples that were being ashed prior to a determination of the phosphorus.

The method which we had adopted for the phosphorus determination in flesh consisted in baking in triplicate about 10 grams of the fresh meat in tared crucibles in an air oven at 110°–120° and then gently igniting in an open crucible over a Bunsen flame to a complete ash. With many of the samples it was necessary to continue the heating eight or ten hours to obtain complete combustion of the organic matter. In spite of the care exercised, some of the samples of ash would fuse and then the particles of unburned carbon could be removed only by heating in the muffle.

The phosphorus was determined on the ash by the usual gravimetric method after digestion with HNO_3 + HCl. Later the Neumann method of digestion with H_2SO_4 + HNO_3 was used. Considerable difficulty was experienced in removing all the ash (especially when fused) from the crucibles. Some of the samples were digested for an entire day.

In order to assure ourselves that the methods employed were reliable, we determined the phosphorus upon another triplicate set of fresh samples, by digesting about 10 grams of the fresh meat exactly as for the nitrogen determinations, neutralizing the excess of H_2SO_4 with strong NH_4OH, and proceeding with the usual gravimetric determinations. These parallel determinations were made upon seventy-two samples from three animals, being the wholesale cuts of the meats (exclusive of bone), the skeleton, and the internal organs. We have averaged the triplicate determinations by the two methods and find that thirty-three of the samples gave higher results by the determination of the phosphorus from the ash, the average result for the thirty-three samples being 0.0133 per cent. above the determinations by digestion with H_2SO_4. Thirty-seven of the samples gave an average of 0.0064 per cent. phosphorus higher by the method of digestion with H_2SO_4 than by the method of ashing. With two of the samples the average of the triplicates was the same for each method.

For the seventy-two samples the method by ashing gives an average of 0.0028 per cent. phosphorus above that obtained by the other method. The greatest excess which the ashing method gives above the other method is 0.0452 per cent., while the greatest excess obtained by the method of digestion with H_2SO_4 is 0.0147 per cent.

		Phosphorus after ashing of sample.			Phosphorus after digestion with H_2SO_4, etc.					
Lab. No.	Description of sample.	*g.*	*h.*	*i.*	*v.*	*w.*	*x.*	Av of *g, h, i.*	Av of *v, w, x.*	Total Av
08.2.10	Digestive and excretory organs	0.2266	0.2234	0.2285	0.2250	0.2233	0.2212	0.2262	0.2232	0.2247
08.2.63	Digestive and excretory organs	0.2043	0.2083	0.2117	0.2181	0.2162	0.2132	0.2081	0.2158	0.2120
08.2.41	Digestive and excretory organs	0.1937	0.1915	0.1929	0.1984	0.1931	0.1914	0.1927	0.1943	0.1935
08.2.18	Lean of round and rump	0.1996	0.1977	0.2019	0.1972	0.1808	0.1895	0.1897	0.1892	0.1945
08.2.71	Lean of round and rump	0.2040	0.2098	0.1994	0.2172	0.2040	0.2122	0.2044	0.2111	0.2078
08.2.90	Lean of round	0.2059	0.2055	0.2083	0.2097	0.2077	0.2111	0.2066	0.2095	0.2081
08.2.20	Lean of loin	0.1944	0.1962	0.1960	0.1932	0.1938	0.1655	0.1955	0.1842	0.1899
08.2.22	Lean and fat of flank and plate	0.1157	0.1172	0.1163	0.1162	0.1134	0.1078	0.1164	0.1125	0.1140
08.2.23	Lean of rib	0.1785	0.1717	0.1773	0.1661	0.1697	0.1665	0.1758	0.1677	0.1718
08.2.55	Liver	0.3331	0.3366	0.3325	0.3302	0.2728	0.2761	0.3341	0.2930	0.3136
08.2.80	Offal fat	0.0336	0.0360	0.0358	0.0353	0.0343	0.0357	0.0351	0.0351	0.0351

In most cases the whole six determinations agree so closely that all the results come easily within the limit of error, and the separation into the two sets of determinations is purely for the purpose of comparison. The preceding table shows a few of the results of the separate determinations.

We can only conclude that, while ignition of meats in a closed muffle causes a loss of phosphorus, the ignition in open crucibles with only a moderate heat will not cause the loss of an appreciable amount of phosphorus. However, as Leavitt and LeClerc[1] have shown, too much care cannot be exercised in the digestion of the ash so as to put all the phosphorus in a form that will be precipitated by the ammonium molybdate. This seems to be most surely accomplished by the Neumann[2] method of digestion with equal volume of sulphuric and nitric acids; or by long (8 to 10 hours) digestion with nitrohydrochloric acid.

Credit is here given Mr. Norman Hendrickson for his assistance in the laboratory work.

COLUMBIA, MISSOURI, June, 1909.

[1] This Journal, **30**, 617 (1908).
[2] *Ibid.*, **24**, 1106 (1902).

ANTI-PUTRESCENT EFFECTS OF COPPER.

By ALFRED SPRINGER, PH D., ASSISTED BY ALFRED SPRINGER, JR

Received May 14, 1909.

Following a discussion before the Cincinnati Section of the American Chemical Society as to whether the peculiar behavior of a certain Cincinnati certified milk, most largely used in that city, warranted the suspicion that it contained an antiseptic, I started a series of experiments both with certified milk and check ones with milk from one of my cows, which I watched carefully so it could not be tampered with. Under like conditions these milks behaved with marked difference. After making several incineration analyses of the certified milk, I found a trace of copper therein, but its presence was not sufficiently conclusive, because the copper chlorides are more or less volatile. I therefore digested a half liter of certified milk with 350 cc. of sulphuric acid in a Kjeldahl flask, heating the same without addition of any extraneous oxidizers twelve days until it had become practically colorless, then drove off almost all of the sulphuric acid. Placing the residue in a beaker, after diluting it with water, I electrolyzed it. The deposit on the cathode was then dissolved in hydrochloric acid, the excess of hydrochloric acid driven off, and then dissolved in water. To this was added potassium ferrocyanide and the iron and copper ferrocyanide separated by means of ammonia. I then filtered out the dissolved cupric ferrocyanide, allowed the excess ammonia to evaporate, and obtained a decided copper reaction with every bottle of certified milk I examined, although the amounts varied considerably. From a half liter of milk the copper and traces of iron which always deposited on the cathode hardly ever weighed more than two milligrams, but generally much less, therefore its exact weight could not be estimated. I then made check experiments with milk from my cow, but could find no copper, although the methods of analysis were exactly similar. In order to convince myself that only to the presence of this substance could be attributed the strange behavior of certified milk, I started a series of experiments first with copper salts, afterwards with copper spirals placed in the milk. While copper salts have been used for antiseptic purposes, their particular application to milk have not received proper attention. Provided these salts or metallic copper come in contact with milk, immediately after milking, most deep-seated reactions take place; however, if the milk is allowed to stand a very short time and become infected with numerous lactic bacteria the cupric salts cannot suppress these unless abnormally large amounts thereof are used.

I observed when ammonium hydrate, in quantities of 0.1 to 0.15 per cent., is added to milk treated with copper salts a reddish brown change of color gradually takes place therein and the underlying liquid becomes turbid. Where no copper is in the milk this change does not take place. This reaction is most pronounced and affords a good test for the detection of copper in milk. Should, however, ammonium hydrate to the extent of more than 0.2 per cent. be added, milks with and without copper gradually assume the reddish brown color, but only those containing copper become turbid. The most marked change produced by the presence of copper is that the milk retains its sweet odor even after the acidity contents are sufficiently high to curdle it. The milk then becomes covered with molds and the odor becomes decidedly nutty without trace of putrescence.

Having now satisfied myself that the certified milk contained copper and having employed methods which indubitably proved its presence, I next determined to find out where and how it was

added to the milk in a manner to escape detection by the Milk Commission; furthermore, whether it was added with the intention to deceive or whether the dairymen were themselves the innocent victims of a process they employed. My son, Alfred Springer, Jr., assisted me in most of the coming experiments and I herewith wish to acknowledge the services rendered by him.

Supplying ourselves with some absolutely clean broad-mouthed glass-stoppered bottles, we went to Lebanon, Aug. 10th, to inspect the dairy in question. We found it a model of cleanliness in every respect. Having the presence of copper uppermost in our minds, we examined the various possibilities of its addition. The Star cooler, made of tinned copper, was the first apparatus that suggested itself as capable of supplying some. An examination thereof showed that the tin had partly worn off at some few places and that the filling valves were made of brass. We then followed the steam pipes used for the cleaning of the bottles, the sterilization of the pails, the straining cloths and the cloths for wiping the udders of the animals. The pipes were iron but all of the gate valves brass.

The superintendent accompanied us through the dairy and willingly complied with all of our requests. We asked that several cows be milked direct into the bottles we had brought along, so that the milk would not come in contact with any utensil they had in the building. This was done and called raw milk. Then we asked for two bottles of milk which, in the usual mode of procedure, had only gone through their straining cloth into the pails. This we called strained milk. We then took two bottles of milk which had passed through the Star cooler. All these bottles were immediately placed in their ice room, then packed in ice and taken to my laboratory; we there subdivided them by running 25 cc. in two-ounce bottles, leaving some closed in the ice-chest and others at room temperature. I also made Kjeldahl digestions of the three kinds. The strained and the certified showed the presence of copper but not so the raw, thus proving that the copper had already entered through the straining cloths and the pails. The raw milk both in the ice-chest and at room temperature, as indicated by titrations with decinormal solutions of sodium hydrate, was much better than the strained or the certified. Both the strained and certified turned the second day at room temperature, the whey separating completely, whereas the raw milk remained sweet three days and then turned normally. In the ice-chest the raw showed great superiority over the strained and certified. These experiments indicated a most undesirable state of affairs, the danger of which cannot be overestimated, namely, that even in a dairy, like that at Lebanon, where all precautions for absolute cleanliness are scrupulously followed, a milk taken directly from the cow, bottled and iced, should be so much superior to others set out from ten to fifteen minutes in the dairy atmosphere. It showed that the atmosphere of the dairy was charged with bacteria and spores of molds which quickly found their way into the milk. We then determined to make a still more crucial test and visited the dairy Aug. 18th, first having supplied ourselves with perfectly clean bottles, which we brought with us. We asked the superintendent to milk six cows, part milked direct into the bottles, part through the straining cloths into the pails, and the rest sent through the Star cooler before any other passed over it. Some of the bottles which had been directly filled were immediately closed and others left open in the dairy fifteen minutes. Furthermore, we took samples of the condensed steam at the washing and sterilizing rooms, also of such used to sterilize the cooler. The various milks, all from the same cows, were taken to my laboratory and subdivided into 152 two-ounce bottles with 25 cc. in each, some set out open, others closed in the ice-chest and at room temperature, some treated with ammonia, and others left for the growth of molds. The results on the charts indicate that an exceptionally good milk direct from the udders of the cow had greatly deteriorated during the short exposure before bottling in the usual mode of procedure.

We examined the samples of water and found that the first one, condensed at the washing room, used to sterilize the bottles, pails and cloths, contained part of the boiler compound mechanically carried over and copper. The condensed water used to sterilize the cooler also showed the presence of copper. We next examined the boiler compound used at this dairy and, strange to say, found that it contained copper salts and was really largely at the bottom of the whole trouble. The priming or passage of foam carried this copper over to the washing and sterilizing room, thus contaminating the cloths, bottles and pails used.

While no exhaustive experiments have been

made to determine whether copper is unsanitary in such small amounts as I found in the certified milk, the very fact that it changes the normal characteristics of the milk should be sufficient for its exclusion. In certified and inspected milk dairies the so-called sterilization processes are produced by means of live steam. In many of these dairies the feed water is hard and the use of boiler compounds becomes necessary; these frequently prime over even through pipes connected with the steam drum. Every ingredient of a boiler compound, whatever it is, ought be rigidly excluded from contaminating the sterilized cloths, pails or other apparatus. This can effectually be done by interposing a still, fed directly with water, and heating it with closed steam from the boiler. This still and all pipes leading to the sterilizing apparatus should be made of block-tin.

While examining the certified milk I made quite a number of experiments with copper salts. The one great fact which always loomed up was that they, even in quantities of one part in two millions, act as antiseptics to putrescent bacteria. Organic matter in solution seldom oxidizes directly to its final stage, but passes through intermediate conditions whereby the more complex forms are broken down. Putrefaction is practically limited to the fermentation of albuminoid substances, and is largely a hydrolytic change caused by the energy of anaerobic organisms, while decay results from aerobic microbial activity.

In order to test the efficiency of copper salts I made the following experiments, keeping check ones without the copper: egg albumin and water, blood albumin and water, egg albumin, pancreatin and water, blood albumin, pancreatin and water; chopped meat in water; eggs placed in cupric sulphate solution; egg and blood albumin with sewage; milk with sewage. In every case the copper salts displayed either greatly retardative or marked inhibitive properties towards the putrefactive bacteria, although in some cases the strength of the solution was insufficient to prevent putrefaction gradually setting in. It seems to me that this property possessed by cupric salts is of great therapeutic value and ought to be carefully studied by competent physiologists.

Diseases owing to the abnormally increased presence of putrefactive bacteria are not uncommon, and heretofore have not been successfully combated by the use of antiseptics. It strikes me that in copper salts we have the means of introducing a substance powerfully antiseptic towards putrefactive bacteria and probably otherwise harmless, which could be administered so as to dissolve in the alkaline mucus, secreted by the intestinal glands, while approaching the colon. Again the antiseptic properties of the copper salts toward the sewage bacteria may be of especial benefit to the dairymen, since so many dairies are located near running streams which, through proximity to large cities, are nothing but open sewers.

OCTOBER 4, '08.

Milk from Springer cow, udders carefully washed, milked in the open and direct in the bottles. First bottle raw, second bottle contained Miami boiler compound 1 : 2500, third bottle contained copper salt, one part copper to 250,000. The bottles were kept cold in ice-chest.

		Raw	Cold boiler compound, 1 : 2500.	Copper. 1 : 250,000.
Oct	5	5.45	5.45	5.45
"	6	5.55	5.55	5.55
"	7	5.6	5.6	5.6
"	8	5.7	5.8	5.8
"	9	5.5	6.15	5.7
"	10	5.85	7.4	5.95
"	12	15.7	8.35	9.00
"	13	23.8	13.1	18.3
"	14	26.5, all but 4 turned	19.5	23.5
"	15	27.0	21.5	25.0
"	16	28.0, all turned	23.0	26.0
"	17	28.5	24.0	27.5
"	19	33.5	29.5, 2 of 5 turned	29.0
"	20	33.5	33.5, all turned	30.2
"	21	34.0	33.5	31.2
"	23	35.0	35.0	32.0
"	24	35.8	35.7	32.5
"	26	37.1	37.0	33.0, 1 in 15 turned
"	27	37.8	37.7	34.0
"	28	38.5	38.4	35.7, half the bottles turned

NOTES AND CORRESPONDENCE.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF MISSOURI.]

LIMITATIONS OF STARCH AS AN ACCELERATOR.

By C. K. FRANCIS.

In the course of several analyses of soils in which the sample was mixed with starch and sodium peroxide and then fused, it was found that the blank gave practically the same percentage of phosphorus as several of the soils. This fact led to an investigation of the starch employed, and upon obtaining a positive test, several other samples of starches were examined. The method of analysis was to digest 5 grams in HNO_3-HCl (30 cc. 10 cc.) to a clear solution, cool, dilute with water, and then determine phosphorus by the gravimetric method.

The results, with name and source of the starch, are shown in the following table

No.	Starch.	Obtained from	Ash, per cent.	P_2O_5, per cent.
96128a	Potato starch	Eimer & Amend	0.292	0.151
" b	" "	" "	0.292	0.159
96129a	Corn starch	" "	0.548	0.036
" b	" "	" "	0.560	0.039
96130a	Bulk corn starch	Ridenour, Baker	0.116	0.043
" b	" " "	Grocery Co., K. C.	0.124	0.047
96131a	Table corn "	Early Breakfast	0.104	0.032
" b	" " "	Coffee Co., St. L.	0.116	0.035
96132a	Wheat starch	Eimer & Amend	0.112	0.089
" b	" "	" "	0.124	0.093
96133a	Soluble starch	Kahlbaum	0.392	0.167
" b	" "	"	0.410	0.169

While the amounts of phosphorus found are relatively small, they are thought sufficient to be considered where starch is employed as an accelerator for sodium peroxide fusions, especially when analyzing certain soils or other materials which contain but traces of phosphorus. As phosphorus was found in all samples of starches examined, sugar has been substituted in its place for the fusion work of this laboratory.

COLUMBIA, MO.

FIRE TEST AS GAUGE OF DANGER FOR KEROSENE.

To the Editor of "The Journal of Industrial and Engineering Chemistry:"

There is a paper on "The Relation between the Temperature of Kerosene and the Explosive Pressure of the Supernatant Mixture of Air and Vapor" by W. P. Bradley and C. F. Hare in THIS JOURNAL, Vol. I, No. 6, June, 1909, p. 345. I read it with great interest. It begins to put the matter on a definite scientific basis.

They criticize fire test as a gauge of the danger of oil. Also I saw in the newspapers that an international committee was to report on methods of oil testing, and among other things on the taking of the firing point. Surely the one duty of scientific men to all present methods of taking the fire test is to condemn them as unscientific and misleading. In a test to indicate the safety or danger of an oil we require one that warns us of the beginning of danger like the Elliot closed flash point and not the much higher figures got in the fire tests. Neither of the fire tests given, Elliot and Tagliabue, "guarantee against danger while the oil is in bulk and kept at a temperature below that of the test." These tests are worse than useless, for the seeming guarantee suggests security and hinders natural precautions and thereby creates or increases danger. For bulk quantities the temperature of the close Elliot flash point is also the point of permanent ignition.

I took a shallow tin dish, circular, 9 inches in diameter, and covered it with a lid having circular holes to test by. An oil that in Abel close cup flashed at 78° F. (25.6° C.), not only flashed but ignited permanently, or fired, at 76° F. or 2° below the closed flash point. Using the same dish without the cover as an open test, applying the flame every 2° it ignited explosively at 88° F. (31° C.) and continued to burn furiously. Tested every degree the firing point was 87° F.[1] The point for flash or fire alters with the amount of oil, and the danger we wish to gauge is not that of cupfuls but the largest quantities in household use, say, large lamps or gallon tins.

The fundamental fact, then, is that for bulk quantities in circumstances where the vapors are allowed to accumulate on the surface of the oil, the closed flash point, Elliot or Abel, is also the fire point.

If the fire point determined in any way is more than 10° F. above the closed flash point then in my opinion the method ought to be condemned as misleading.

In England, shops and cellars have often been burned in hot weather by the kerosene, which was being sold, accidentally catching fire and burning furiously, flash point between 73° F. (23° C.) and 80° F. (27° C.), and not infrequently the flame has run along the heavy vapor some distance to the oil.

If an international or other scientific committee takes up the matter of fire test, I hope they fix on one that aims at what professes to be *the minimum* temperature of permanent ignition; and that for at least the largest quantities in common household use. But I think the fire test should be done away with and only the flash point used and all dangers referred to that standard. D. R. STEUART.

BROXBURN, SCOTLAND,
July 5, 1909.

[1] *Chemical News*, June 3, 1893, and *Journal of Society of Chemical Industry*, **15**, 173 (1896).

MOISTURE CONTENT OF BUTTER.

Editor, Journal of Industrial and Engineering Chemistry:

I have read with interest the Note of Mr. F. W. Robison in the May number of THIS JOURNAL, on "Variation of Moisture Content in Butter, Etc.," and as I differ quite decidedly would like to note a few points.

Butter, as every one knows, is not a homogeneous mixture, the content of water, curd, salt and fat varies in every portion of a mass of butter from any other portion of that mass. The better the butter is made, the closer will the different constituents agree. Butter containing more than 15.99 per cent. of water is considered adulterated by the Federal Government, and it is my experience that all butter handlers consider this a fair limit

Thousands upon thousands of tubs of butter are sampled each year by the Revenue Officers, and the question of sampling has been a very important one. In the only case under the law where a creamery has sued the Government to recover the tax assessed for manufacturing adulterated butter, the testimony shows that the Revenue Agent in taking the samples used a trier for the first tub in the presence of the President of the Creamery and the butter-maker. The trier had been thrust one or more times into the tub when the creamery people objected and asked the officer to take the samples with a ladle, and not use the trier as the tubs of butter after being punched five or six times with a trier would not have much of a market value. The officer complied, and the remaining samples were taken with a ladle furnished by the creamery, yet when they protested against the assessment and the case came into the Federal Court, the cry was raised that the samples were not taken with the trier, and were unfair. (The Government won the case.)

While assisting a Revenue Agent take some samples with a trier, I asked the Commission Merchant if he had trouble selling butter which had been sampled with a trier; he said: "Oh I will sell this one tub but will never sell another to the same man."

The Revenue Office has received so many complaints about sampling with a trier that the method had to be abandoned in the interest of the entire butter industry, as it is the universal statement of the butter trade that every tub of butter sampled with a trier by a Revenue Officer for moisture is ruined as far as its sale as table butter is concerned.

The instructions now are to take a sample from the top of the tub and one from the bottom, combine the two into one sample, or to take two samples from opposite parts of the sides of the tub and combine them. Our experimental work proves this method to give as fair a result for the tub as any possible method. The only complaint I have ever heard against this method of sampling butter, came from the above-mentioned creamery people, who wanted this method used when the samples were being taken, but who cried "unfair" when the case came into Court.

Respectfully,
A. B. ADAMS.

CHIEF, DIVISION OF CHEMISTRY,
BUREAU OF INTERNAL REVENUE.

BOOK REVIEWS AND NOTICES.

Sprechsaal Kalender for the Ceramic, Glass and Allied Industries. J. KOERNER. 115 pp. Mueller & Schmidt, Coburg.

This publication of 115 pages is one of the most unique attempts in chemical technology. It summarizes all of the recent work done in Germany in the field of silicates, paying particular attention to the accurate, scientific researches such as the work of Berdel on the vitrification of clay substance, quartz and feldspar, insoluble glazes, testing of glass, Rieke's researches on mica, lime, magnesia and titanic acid, Simonis' results on ternary mixtures of kaolin, quartz and feldspar, etc. In addition a good deal of general information is given regarding bodies, glazes and glass which is very useful. Dr. Koerner is to be congratulated in producing such a radical change in the make-up of such a publication, and it is to be hoped that this feature will be maintained in the future and include also the results of American research along these lines. A. V. BLEININGER.

The Testing and the Properties of Sand-Lime Bricks. H. BURCHARTZ. Royal Materials Testing Station, Gross Lichterfelde. 105 pp. Julius Springer, Berlin.

Exhaustive tests and statistics on the properties of these bricks. This work is probably the most thorough ever done in this field. The recommendations for specifications governing the purchase of sand-lime bricks are especially interesting and are as follows: The bricks must possess good structure and must have a good ring. The water absorption should not be more than 15 per cent. of the weight of the dry brick. When used as backing up bricks or as facing they should have a crushing strength of not less than 2100 pounds per sq. inch; the regular run of hard brick should show a crushing strength of not less than 2800 pounds per sq. inch, tested in the dry condition. The bricks must not soften in water and the crushing strength when tested wet should not be lower than when tested dry by more than 15 per cent. They must resist 25 successive freezings. The loss in crushing strength on freezing should not be more than 20 per cent. as compared with the dry strength. The crushing strength to be accepted should be the average of 10 tests. Variations amounting to 10 per cent. below the minimum requirements in strength are permissible.

A. V. BLEININGER.

NEW BOOKS.

This list was prepared by Mr. Paul Escher, 1319 Pearl Street, Alameda, Cal.

Food Chemistry.

Kakao und Schokolade. By E. LUHMANN. 1909. kl. 8°. 210 pp., 68 Abb. Hannover. Mk. 4, Lnbd. 4.40.

Neue Arzneimittel u. Pharmazeutisch Spezialitäten. By G. ARENDS. 3 A. kl. 8°. VIII, 681 S. Berlin, 1909. Lnbd. M. 6.

Volksernährungsfragen. By MAX RUBNER. Leipzig, Akademische Verlagsgesellschaft m. b. H., 1908. 143 Seiten.

Uebersicht üb. die Jahresberichte der öffentl. Anstalten zur technischen Untersuchung v. Nahrungs- u. Genussmitteln im Deutschen Reich. 1905. Lex. 8°. VIII, 348 u. 45 S. Berlin, 1909. Mk. 7.60.

The Canning of Peas, Based on Factory Inspection and Experimental Data. By A. W. BITTING. Food Inspector, Bureau of Chemistry. pp. 32, figs. 6. (Bulletin 125, Bureau of Chemistry.) Price, 10 cents.

The Influence of Acidity of Cream on the Flavor of Butter. By L. A. ROGERS and C. E. GRAY. pp. 22. (Bulletin 114, Bureau of Animal Industry.) Price, 10 cents.

The Influence of Sodium Benzoate on the Nutrition and Health of Man. By IRA REMSEN and ASSOCIATES. pp. 784, charts 4. Referee Board of Consulting Scientific Experts. (Report 88, Office of the Secretary.) Price, $1.00.

The Science and Practice of Cheese Making. By L. L. VAN SLYKE and C. A. PUBLOW. 12°. 16, 483 pp. New York, 1909. Cloth, d. 1.75.

Beiträge zur Synthese der Fette. By P. SCHACHT. Symmetrische Glyceride. 8°. 60 S. Diss., Zurich, 1908.

Handbuch der Drogisten-Praxis. By G. A. BUCHHEISTER. 1 Teil. 9. Aufl. gr. 8°. IX, 1115 S. m. 352 fig. Berlin, 1909. Mk. 12, Lnbd. 13.40.

Practical Physiological Chemistry. By P. B. HAWK. 2nd ed. 8°. London, 1909. 16 sh.

American Medicinal Barks. By ALICE HENKEL. Assistant Drug-Plant Investigations. pp. 59, figs. 45. (Bulletin 139, Bureau of Plant Industry.) Price, 15 cents.

Fermentation Chemistry.

Anleitung zur Biologischen Untersuchung u. Begutachtung Von Bierwürze, Bierhefe, Bier u. Brauwasser, zur Betriebskontrolle Sowie zur Hefereinzucht. By H. WILL. XVIII u. 482 S. m. 84 Abb. u. 3 Taf. Munchen, 1909. Lnbd. 12 Mk.

Handbuch des Weinbaues u. der Kellerwirtschaft. By A. FRHR. V. BABO and E. MACK. 1. Bd. Weinbau. 3 A. Hrsg. v. K. Mader u. F. Zweifler. 1. Halbbd. gr. 8°. XX, 623 S. Berlin, 1909. Lnbd. 16 Mk.

Agricultural Chemistry.

Die Destillation Industrieller und Forstwirtschaftlicher Holzabfälle. By W. B Harper. Deutsch von R. Linde. 1909. Berlin, J. Springer. Mk. 10, geb. Mk. 11.

Landwirtschaftlich-Technische Nebengewerbe. By K. Steinbruck. Kl. 8°. VIII, 59, IX, 160, IX, 134, VI, 130, VIII, 89 u. VII, 59 S. m. Abb. u. 5 Taf. Hannover, 1909. Lnbd. 7 Mk.

Fumigation Investigations in California. By R. S. Woglum. Special Field Agent. pp. 73, Figs. 28. (Bulletin 79, Bureau of Entomology.) Price, 15 cents.

Proceedings of the Twenty-Fifth Annual Convention of the Association of Official Agricultural Chemists, Held at Washington, D. C., November 12-16, 1908. Edited by Harvey W. Wiley, Secretary of the Association. pp. 248, figs. 6. (Bulletin 122, Bureau of Chemistry.) Price, 40 cents.

Die Fabrikation des Superphosphats M. Berücksichtigung der Anderen Gebraüchlichen Düngemittel. By L. Schucht. 3 A. gr. 8°. VIII, 460 S. m. 153 Abb. u. 4 Taf. Braunschweig, 1909. M. 18, gebd. 20.

Die Vermehrung der Kaliwerke u. der Kaliabsatz. By H. Münster. Halle a/S, 1909. M. 3.60.

Electrochemistry.

Die Elektrochemischen Verfahren der Chemischen Grob-Industrie. By J. Billiter. Bd. I. Elektrometallurgie wässriger Lösungen. Halle a/S, 1909. 12.

Elektrochemie Geschmolzener Salze. By R. Lorenz and E. Kaufler. Lex. 8°. VI, 84 S. m. 17 Abb. Leipzig, 1909. 3.60.

Calcium-Carbid und Seine Volkswirtschaftliche Bedeutung F. Deutschland. By W. Le Coutre. Berlin, 1909. Mk. 3.

Production Electrique de L'Ozone et Applications A L'Industrie, L'Hygiene, La Therapeutique. By E. Douzal. 8°. Ill. Paris, 1909. Fr. 15.

Analytical Chemistry.

Ueber die Anwendung der Thermischen Analyse zum Nachweis Chemischer Verbindungen. By R. Kremann. Lex. 8°. 76 pp. 43 Abb. Stuttgart, 1909. Mk. 2.40.

Logarithmische Rechentafeln für Chemiker, Pharmazeuten, Mediziner und Physiker. By F. W. Küster. 9th Aufl. 12. Leipzig, 1909.

Einrichtung von Laboratorien und Allgemeinen Operationen. By V. Samter. Halle a/S, 1909. Mk. 2.70.

Laboratoriumsbuch F. die Industrie der Verflüssigten u. Komprimierten Gase. By K. Urban. Gr. 8°. VIII, 40 S. m. 24 Abb. Halle a/S, 1908. 1.80

Coal, Fuel and Petroleum.

Analyses of British Coals and Coke, and the Characteristics of the Chief Coal Seams Worked in the British Isles. By A. Greenwell and J. V. Elsden. 3rd ed. 4°. London, 1909. sh. 10.

Tests of Coal and Briquets as Fuel for House Heating Boilers. By D. T. Randall. 8°. 44 pp. London, 1909. 1 sh. 6 d.

Das Erdöl. Hrsg. v. C. Engler u. H. Höfer. 2 Bd. Die Geologie, die Gewinnung und der Transport des Erdöls. Lex. 3. 992 S. m. 307 Abb. u. 26 Taf. Leipzig, 1909. Mk. 46, Hlbfrz. 50.

Explosives.

Explosivstoffe, auf Grund des in der Literatur Veröffentlichten Materials Bearbeitet. By H. Brunswig. 1909. 177 pp. 45 Fig. 56 Tab. Leipzig. Mk. 8, geb. Mk. 9.

Lustfeuerwerkerei für Berufsfeuerwerker und Leibhaber. By H. Falbesoner. Mit 391 verschiedenen Kompositionen u. Angabe der Bereitung aller im Handel schwer erhaltl. Präparate. gr. 3. 256 S. m. 100 Abb. Wien, 1909. 5, gebd. 6.

Photography.

Das Arbeiten Mit Farbenempfindlichen Platten. By E. König. (Photogr. Bibl. 25 Bd.) 8°. VII; 76 S. m. Fig. im Text u. 16 Taf. Berlin, 1909. 2.25, gebd. 2.85.

Water and Water Supply.

The Disinfection of Sewage and Sewage Filter-Effluents. By E. B. Phelps. 1909. Water-Supply Paper No. 229, U S. Geol. Surv., Washington.

Technical Chemistry.

Wasch-, Bleich-, Blau-, Stärke- und Glanzmittel. By L. E. Andes. 1909. 384 pp. 21 Abb. Wein, Mk. 5, geb. Mk. 5.80.

Practical Electroplating: A Guide for the Electroplater. By W. L. D. Bedell. 12. 244 pp. Newark, 1909. Cloth, $2.00.

Das Salz, Dessen Vorkommen und Verwertung in Samtlichen Staaten der Erde. By J. O. Frhr. v. Buschmann. I. Bd. Europa. Lex. 8°. 784 S. Leipzig, 1909. 26, Hlbfrz. 30.

Die Starkefabrikation. By J. Schmidt. (Bibl. d. ges. Landwirtschaft. 39 Bd.) IX, 134 S. m. 44 Abb. u. 5 Taf. Hannover, 1909. Mk. 2.20, Lnbd. 2.50.

Betrachtungen ub. die Bewegende Kraft des Feuers u. die zur Entwicklung Dieser Kraft Geeigneten Maschinen. By S. Carnot. (1824). Ubers. u. hrsg. v. W. Ostwald. (Ostwald's Klassiker d. exakt. Wissenschaften Nr. 37) 2. A. 8. 72 S. m. 5 Fig. Leipzig, 1909. 1.20.

Air Liquide, Oxygene, Azote. 8°. 403 p. av. fig. Paris, 1909. Fr. 15.

L'Industrie Des Parfums D'Apres Les Theories de la Chimie Moderne. By M. Otto. Notations et formules. Les parfums naturels. Les parfums artificiels. 8°. VIII, 545 pp. av. fig. et portr. Paris, 1909. Broche Fr. 22.50.

Handbuch der Farbenlehre. By E. Berger. 2 A. kl. 8. XIV, 304 S. m. 36 Abb. u. 8 Taf. Leipzig, 1909. Lnbd. Mk. 4.50.

Metallurgy and Geology.

Metallurgical Calculations. By J. W. Richards. Part III The Metals Other than Iron (Non-ferrous Metals.) 8°. New York, 1908 (1909)

Welding and Cutting Metals by Aid of Gases or Electricity. By L. A. Groth. 8. London, 1909. 19 sh. 6 d.

The Preservation of Iron and Steel. By Allerton S. Cushman. Assistant Director, Office of Public Roads. pp. 40, pls. 4. (Bulletin 35, Office of Public Roads.) Price, 10 cents.

Radioactivity and Geology. By J. Joly. 8. London, 1909. 7 sh. 6 d.

Bibliography of North American Geology for 1906 and 1907. By J. M. Nickles. With subject-index. 1909. Bull. 372, U. S. Geol. Surv., Washington.

Miscellaneous.

Kapillarchemie. By H. Freundlich. Eine Darstellung der Chemie der Kolloide und verwandter Gebiete. Gr. 8°. 600 S. m. 93 Fig. u. Kurv. Leipzig, 1909. 16.30, gebd. 17.50.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY LONDON, MAY 27th TO JUNE 2nd, 1909.

Report of Section VIII C.

Bromatology.

Friday, May 28th, President R. R. Tatlock.

"The Systems in Force for the Control of the Food Supply." This subject was discussed by Dr. Wiley, America, Dr. Roun and Dr. Bordas, France, and Dr. Buchanan, Great Britain. Further discussion was postponed until additional papers were read on Monday the 31st at 10 A.M.

Saturday, May 29th, President Dr. Bordas.

The morning was devoted to reports and discussion by the International Commission for the Unification of Analytical Results.

Monday, May 31st, President Dr. Bordas.

The discussion of the subject "The Systems in Force for the Control of the Food Supply" was continued by Dr. Wauters, Dr. Kerp, Dr. McGill, Prof. Schaffer, Prof. Wysman and Dr. Van Rijn. Drs. Thorpe, McKerp and Blitz also discussed the subject. Papers on milk analysis were presented by Mr. Taffe, Messrs. Russell and Armaud and Dr. Bordas.

The International Commission on the Unification of Analytical Methods reported that several meetings had been held and a plan of organization adopted. Methods of analyses prepared by Messrs. André, von Buchka, Chapman, Cribb, Lavalls, Schoepp, Mastbaum, Pintti, Vandevelde, Wauters and Wiley were reported. Several new members were added to the commission and the following officers elected: M. von Buchka, *President;* Messrs. Gautier, Thorpe, Pintti, Schaffer, Wauters, Wiley, Wysman, *Vice-Presidents;* and Mr. Vandevelde, *General Secretary.*

P.M., Dr. Bordas, President.

Papers on the composition of brandy and other spirits were read and discussed. The following resolution was adopted "That brandy is a product of the distillation of wine, and the term is synonymous with eau de vie de vin."

Tuesday, June 1st, 10–12.30 A.M., Presidents, Prof. Wysman, M Wauters, Dr. Buchka.

F. W. Beck read a paper "On the Advantages and Disadvantages of Legally Binding Standards for Foods and Drugs" This was generally discussed and at 12.30 the Section adjourned to be photographed.

12.45 1.30, Joint Meeting with Section I (Chocolate). Presidents Dr. Klop, Prof. Wysman.

Several papers dealing with cocoa and chocolate were presented.

P.M., 4–6, Presidents Dr. McGill, Dr. Buchanan, Mr. Ferriers.

Papers on "The Use of Preservatives in Food" by Mr. Bevan, Dr. Thresh and Dr. Wiley were read and discussed. The Section adjourned at 5.30 *sine die.*

F. C. Cook.

RECENT PATENTS.

The following patents relating to industrial and engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, 908 G Street, N. W., Washington, D. C.

922,494. **Process of Making Fertilizing Material.** John W. Lowman, Nashville, Tenn. May 25, 1909.

This is a process of producing a phosphatic fertilizer, by pulverizing a predetermined amount of phosphate material, burning and pulverizing a predetermined amount of dolomite or magnesia limestone, burning and pulverizing a predetermined amount of fluor-spar, thoroughly mingling all of the said substances, adding a predetermined amount of potash thereto, reducing the product thus formed to a plastic mass by stirring water thereinto, and then heating the said mass.

922,523. **Flux for the Autogenous Welding of Aluminum.** Max U. Schoop, Bois, Colombes, France. May 25, 1909.

The flux consists of chloride of potassium, chloride of sodium, bisulphate of potassium and chloride of lithium.

923,005. **Process of Treating Nickle Ores.** Anson G. Betts, Troy, N. Y. May 25, 1909.

This is a process of treating an ore containing a metal of the iron group, by smelting to an alloy with another metal of the iron group, and electrolytically refining the alloy, using an electrolyte containing a soluble salt of each of such two metals, and producing a refined alloy containing the said two metals.

923,152. **Silicon Alloy.** John T. H. Dempster, Schenectady, N. Y. Assignor to General Electric Company, a corporation of New York. June 1, 1909.

The alloy consists of silicon and tellurium.

923,228. **Method of Insulating Sheet Metal.** Willis R. Whitney, Schenectady, N. Y. Assignor to General Electric Company, a corporation of New York. June 1, 1909.

The process consists in coating a sheet-metal plate with a colloidal suspension of gum copal and then heating said plate to produce a uniform adherent coating of gum copal.

923,232. **Process for Making Alcohol.** Adolph Woolner, Jr., and Aladar Lassloffy, Peoria, Ill. Assignors to Woolner Distilling Company, Peoria, Ill., a corporation of Illinois. June 1, 1909.

This is a process for the manufacture of alcohol consisting in growing in distillery shop fungi having diastatic properties, combining the same with a malt converted mash and distilling the mixture after fermentation.

923,358. **Non-conducting Compound.** Franc J. Jewett, New York, N. Y. Assignor to H. W. Johns-Manville Company, a corporation of New York. June 1, 1909.

This is a composition of matter for use in heat insulation

comprising short asbestos fiber, granulated cork, disintegrated sponge treated with a boron compound and infusorial earth.

923,411. **Manufacture of Zinc Dust.** SHERARD O. COWPER COLES, London, England. June 1, 1909.

The process consists in electrodepositing zinc from a caustic soda solution upon a revolving disk upon which the disk is deposited in the form of a sponge and is continuously removed, and in then drying the spongy zinc so produced in a reducing atmosphere.

923,427. **Process of Treating Petroleum Sludge to Produce Pitch, Asphalt, Etc.** JOHN L. GRAY, Elizabeth, N. J. June 1, 1909.

The process consists in digesting the sludge until the major part of the acid has been removed, and then slowly heating.

923,428. **Process of Treating Petroleum Sludge.** JOHN L. GRAY, Elizabeth, N. J. June 1, 1909.

This is a process of separating the constituents of petroleum sludge into various grades by pumping off any mechanically entrained oil which may rise to the top, digesting the sludge until the light constituents including the unsaturated hydrocarbons rise to the top, withdrawing this by-product and the acid, then digesting again until the lighter grade rises, removing that grade and the acid, and so continuing until there remains a solid residuum.

923,429. **Process of Separating Acid from Petroleum Sludge.** JOHN L. GRAY, Elizabeth, N. J. June 1, 1909.

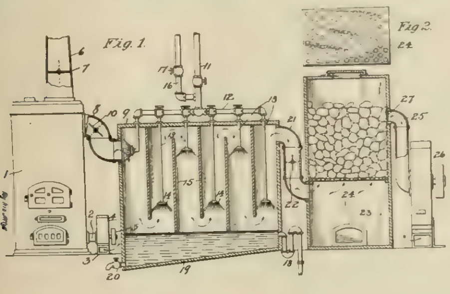
The process consists in washing or digesting the sludge with a weak acid solution.

923,581. **Process for the Production of Carbon-Covered Metal Sheets for Dynamo-Brushes.** JOHANNES F. P. RINGSDORFF, Essen-on-the-Ruhr, Germany. June 1, 1909.

The process consists in smearing a carbon paste on the surfaces of said metal sheets and subjecting them to hydraulic pressure.

923,846. **Process of Extracting Nitrogen from Air.** OLIVER P. HURFORD, Chicago, Ill. June 1, 1909.

This process is practiced by the use of the apparatus illustrated, in which carbonaceous fuel is burnt in the furnace shown at the left of the illustration, air being admitted in amounts sufficient for complete combustion. The gaseous products of combustion which are free from carbon monoxide enter through a chamber where they are subjected to the action of lime water to absorb the carbon dioxide and the nitrogen being dried by the means of lime or other drying agent is drawn off for use.



923,864. **Process for the Electric Dissociation of Metals by the Wet Method.** June 1, 1909.

This is an electrolytic process for cleaning metal articles and subsequently coating them with metal which consists in placing the article to be coated in a bath consisting of a concentrated alkaline solution and an alkaline cyanide, placing in the solution a quantity of the metal of the kind of which the coating is to be formed, and connecting both the article and the coating metal to a suitable source of electricity, the former as a cathode and the latter as the anode

923,891. **Manufacture of Bituminous Roadways.** CLIFFORD RICHARDSON, New York, N. Y. Assignor to the Barber Asphalt Paving Co., Philadelphia, Pa., a corporation of West Virginia. June 8, 1909.

This is a process of preparing bituminous paving material which consists in employing a mineral aggregate of two sizes, the one consisting of No. 2 stone and the other screenings from three-eighths of an inch to dust, the latter being proportioned to fill the voids of the former; adding to the large sized material while cold a hot bituminous cement in amount more than sufficient to coat the stone; thoroughly mixing; and then adding the finer material

923,916. **Method of Thionous Precipitation.** GEORGE C. WESTBY, Murray, Utah. June 8, 1909.

This is a method of precipitating copper or silver from their solution by means of the addition of a liquor containing thio salts of iron.

923,967. **Process of Producing Camphene.** CHARLES GLASER, Baltimore, Md. June 8, 1909.

The camphene is produced from bornyl chloride by the distillation of that substance at a temperature between 180° and 210° C. and for a time refluxing the distillate, then separating the distillate and collecting it.

923,076. **Process for Obtaining Pure Copper.** LUCIEN JUMAU, Paris, France. June 8, 1909.

The process consists in obtaining pure copper from a solution of a salt of copper, by subjecting said solution to the action of carbon monoxide in a closed receptacle, and heating the solution during such treatment.

923,077. **Process for Obtaining Pure Metallic Copper from a Solution of Salt and Copper.** LUCIEN JUMAU, Paris, France. June 8, 1909.

The process consists in obtaining copper from a solution containing salts of copper and subjecting said solution to heat and pressure, in the presence of a reducing agent containing hydrocarbons.

924,677. **Process of Smelting Iron Oxides.** HORACE W. LASH, Cleveland, Ohio. June 15, 1909.

The process consists in charging into a furnace a smelting mixture containing finely divided cast iron and carbonaceous material, and distributing in the mass of the smelting mixture chunks or masses of pig metal and applying a smelting heat to the charge.

924,770. Art of Treating Wood for Lumber. WILLIAM A. HALL, New York, N. Y. Assignor to American Mahogany Company, a corporation of Maine. June 15, 1909.

The wood is impregnated with an alkalized solution of the phlobaphenes of the hemlock bark, which solution contains an excess of alkali over that necessary to dissolve the phlobaphene extract.

924,818. Process of Producing High-grade Steel from Low-grade Material. WILLIAM R. PALMER, Bridgeport, Conn. Assignor one-half to Frank A. Wilmot, Bridgeport, Conn. June 15, 1909.

The process consists in charging a primary furnace, with low-grade material of the character described, operating said furnace at a temperature below ordinary steel-making temperature, partially charging a secondary furnace with scrap and flux, operating said furnace at ordinary steel-making temperatures, transferring a portion of the charge from the primary furnace to the secondary furnace for the completion of the refining operation, and returning a portion of the charge to the primary furnace to form a bath to receive the next charge of the low-grade material.

925,253. Process of Making Ammonia and Chlorin or Hydrochloric Acid. NORMAN L. WHITEHOUSE, Lewisham, London, England. June 15, 1909.

This is a process for obtaining chlorine from ammonium chloride consisting in heating at a low temperature ammonium chloride with an oxide of a rare earth metal, adapting to expel ammonia from ammonium chloride at that temperature and then heating the residue at a higher temperature in an atmosphere adapted to expel chlorine from a chlorine compound of a rare earth metal at the said higher temperature.

925,321. Process for Facing Stereotype Metal. WILLIAM R. FISHER, San Francisco, Cal. Assignor one-third to Joseph F. Moran, San Francisco, Cal. June 15, 1909.

The process consists in facing stereotype and like plates with a protecting metal by first washing the plate in caustic potash, then placing it in a bath of potassium cyanide, again washing the plate and placing it in a solution of platinum cyanide, and subsequently applying the facing metal by electro-deposition.

925,365. Metallization of Vitreous Ceramic Surfaces. QUENTIN MARINO, London, England. Assignor three-fourths to Edwin Joseph Richardson, London, England. June 15, 1909.

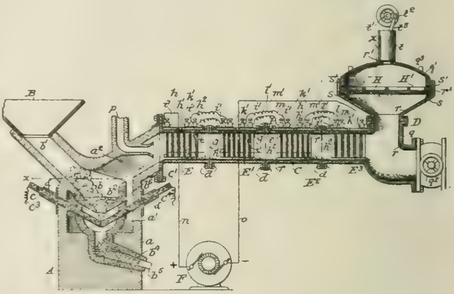
The metallizing of the ceramic surface is accomplished by applying thereto a solution resulting from dissolving in hydrofluoric acid a gray substance consisting of filiform silver and basic nitrate of copper, and then, while the surface is wet with the solution, dusting said surface with a metal in a finely divided state and such as will reduce the silver and copper in the fluoride to a metallic state.

925,612. Refining of Steel in Electric Furnaces. OTTO THALLNER, Bismarckhutte, Germany. Assignor to The Firm of Bismarckhutte, Bismarckhutte, Germany. June 22, 1909.

This is a process for producing high-quality steel by preliminary refining of the steel in a fuel-heated furnace, then passing the steel so refined for treatment in a basic-lined electric furnace, after which the steel is passed to an acid-lined electric furnace.

925,626. Apparatus for Recovering Metals from Ores and Other Substances. LEON DION, New York, N. Y. Assignor to the American-Hermatic Company, New York, N. Y., a corporation of Arizona. June 22, 1909.

In the treatment of ores to recover the metals contained in them, part of the metal passes off, in the form of fumes or vapors, when the ores or other substances containing them are subjected to the required heat to fuse them. The metal or metals thus carried off in the shape of fumes, gases or vapors may be concentrated or condensed, and thereby recovered or reclaimed, by subjecting these latter to the



action of an electric current supplied through appropriate electrodes, the result of which is to cause the particles of metal contained in or forming the fumes, or vapors of each to cohere and form masses of appreciable size, which are then thrown down or precipitated by the action of gravity or otherwise and may be recovered in that form. The apparatus illustrated is designed for use in carrying out this process, the metal-laden fumes being subjected to the action of a suitable electric current to precipitate the metal.

925,670. Composition for Oxidizing and Purifying Explosive Gases. HERBERT WALKER KNIGHTS, Transvaal. June 22, 1909.

This is a composition for destroying the noxious or poisonous fumes or gas arising during the blasitng in mines, consisting of permanganate of potassium, chloride of ammonium, and chlorate of potassium

926,280. Process of Preparing Concentrated Hydrated Magnesia. WINFIELD S. MORRISON, Oakland, Cal. June 29, 1909.

The process consists in preparing a concentrated magma of magnesium hydroxide, by agitating and boiling the magma with a separate portion of water and settling each day for several days and then straining to remove the surplus water.

926,289. Process for Desulfurizing and Agglomerating Ores. CYRUS ROBINSON, Mount Vernon, N. Y. June 29, 1909.

The method consists in continuously desulfurizing ores, by continuously subjecting successive layers of moving ore to the action of heat in an oxidizing atmosphere without the use of extraneous fuel.

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EDITORIALS.

THE MOISTURE DETERMINATION.

THAT scientific training and thought do not eliminate altogether the judgment based on sentiment, custom and tradition is true, yet nevertheless the man of scientific habits is probably on the whole freer from unreasoned and snap judgment than the average man. The remains of these things in him link him to the past and the conservation of heredity and custom prevent his too-rapid evolution.

The necessity for standard methods of analysis worked out and followed in greater or lesser detail by chemists is everywhere recognized. Their greatest drawback is that they tend to make the analyst more of a machine and less of a reasoning being. A method once adopted and generally recognized attains with use and age a peculiar prestige. Results obtained by it, not infrequently go unquestioned and unchallenged by the analyst. Such a method is the moisture determination "at the boiling point of water." This, the least accurate of methods, as ordinarily performed, is considered by the majority of chemists to yield all but perfect results. It is a strange commentary on analytical chemistry that of the two commonest substances on the earth, water and oxygen, the one is ordinarily determined with a very low degree of accuracy and the other not determined at all.

The Association of Official Agricultural Chemists directs that the moisture in fertilizers be determined by heating 2–5 grams of the sample for five hours at the temperature of boiling water. The loss of weight is reported as moisture. The National Fertilizer Association sent out, some time ago, four check samples of phosphate rock which were analyzed by some thirty-two chemists. On sample No. 1 the returns for moisture showed: average 1.10 per cent., maximum 1.50, minimum 0.69, difference 0.81; sample No. 2 average 0.48, maximum 0.73, minimum 0.25, difference 0.48; sample No. 3 average 0.56, maximum 0.87, minimum 0.27, difference 0.60; sample No. 4 average 0.31, maximum 0.60, minimum 0.06, difference 0.54. These are enormous differences for small percentages and of course would not be tolerated in many kinds of analysis.

Instances might be multiplied. Stranger figures than those given above have been yielded in coöperative work on coal, meat extracts, fertilizers, stock foods and organic and inorganic materials of the most varied sorts. The inaccuracies are great enough to warrant attention and invite correction. They are of every-day occurrence in industrial and commercial laboratories. They may be positive or negative, resulting from loss of volatile substances other than water, or from the addition of oxygen by the oxidation of fats and oils and other readily oxidized substances.

In spite of the known insufficiency of the moisture determination by loss, even in the case of check samples sealed with all precautions chemists are accustomed to calculate results to the "dry basis," when differences in other determinations occur, for purposes of comparison. This is worse than

folly and adds error to error. It would seem that the inaccuracy of the ordinary moisture determination should be recognized although sanctioned officially. This is the least thing which could be asked or done. If it is necessary to have and use methods of a low order of accuracy, the fact ought to be well understood, clearly recognized and the methods used for what they are worth and no more.

ORIGINAL PAPERS.

THE BAG HOUSE AND ITS RECENT APPLICATIONS.

By W. C. Ebaugh

Received August 20, 1909.

The recovery of dust and fume from metallurgical operations is one of the most important problems confronting the works' manager. Escaping fume means loss in efficiency of metal extraction and becomes the cause of injury to surrounding property, thereby resulting in suits for damages or for injunctions. The literature relating to smoke damage[1] is quite extensive, and the numbers of lawsuits in California, Montana, Tennessee and Utah growing out of the question need only to be drawn to our attention in order to impress us with the magnitude of the subject. An excellent résumé of the legal status of the smoke question is given in a recent number of the *Engineering and Mining Journal*.[2]

In his testimony before the Federal Court for the District of Montana Mathewson gave the following summary of the methods that have been tried to remove fume from smoke:[3]

A.—Cooling processes.
1. Water spray.
2. Admission of air.
3. Radiation.
4. Freezing.

B.—Filtering processes.
1. Bag house.
2. Friction.
3. Centrifugal gas cleaners.

C.—Electrostatic process.
1. Cottrell process.

For reasons that need not be discussed here the cooling processes enumerated above have not been satisfactory when applied to lead and copper smelter smoke. The Cottrell electrostatic process is still in an experimental stage. Greater success has attended the various filtering processes. The Theisen centrifugal purifiers[1] and the Osborn purifiers combine the centrifugal action with water spray, and are successful in removing dust from gases, but experiments made in the Salt Lake Valley indicate that such processes do not remove the fume from lead and copper smelter smoke. The various friction devices, such as Cowper flues, Freudenberg plates, Roesing screens, zigzag flues, etc., also seem to aid in settling the dust, but not in removing fume. It is said that by permitting flue gases to enter expansion chambers[2] the solids can be settled out if the velocity be reduced sufficiently, but here too the fume escapes. In fact when treated by any of the above mentioned methods the minute particles that constitute the fume seem to act more like insoluble gases than like solids.[3]

For lead and zinc furnaces the bag house has long been recognized as a most efficient means for removing solids from smoke. Beginning with the work of Jones,[4] who used large bags (8x70 ft.) for filtering zinc fume, Wetherill, and Hall,[5] who substituted screens in the side of a house for the bags previously employed as filters, we find Percy[6] suggesting that a fabric might be used for lead fume. The inventions of Lewis and Bartlett (1878, *et seq.*), Ward,[7] Batchman[8] and Bartlett[9] led up to the modern bag house as perfected by

[1] See bibliographies in "Rauch-beschädigung," Haselhoff und Lindau (Borntrager, Leipzig), pp 395-400, Persifor Frazer, *Trans A. I. M. E.*, **38**, 520–555 (1907); Haywood, *Bulletins* **89** and **113**, *Bureau of Chemistry, U. S. Dept. of Agric.*; Haywood, *Jour. Amer. Chem. Soc.*, **29**, 998-1009 (1907); Ebaugh, *Jour. Amer. Chem. Soc.*, **29**, 951–970 (1907); Harkins and Swain, *Jour. Amer. Chem. Soc.*, **29**, 970–998 (1907); **30**, 915–946 (1908); Widtsoe, *Bulletin* **88**, *Utah Agri. Expt. Sta.*

[2] Baskerville, *Eng. Min. Jour.*, **87**, 884-886 (1909).

[3] *Eng. Min. Jour.*, **87**, 87 (1909).

[1] *Eng. Min. Jour.*, **70**, 607 (1900).

[2] *Ibid.*, **80**, 695 (1905).

[3] The difference in composition between the dust deposited in a flue at a given point and the fume (probably mixed with dust) drawn from the flue at the same point and collected by bag filtration is shown by the following analyses:
(*a*) Fume from copper blast furnaces.
(*b*) Dust from copper blast furnaces.
(*c*) Fume from copper converters.
(*d*) Dust from copper converters.

Sample number	*a*	*b*	*c*	*d*
Density in lbs. cu. ft.	12.75	77.0	not determined	
Gold in ozs./ton	0.16	0.33	0.20	6.0
Silver in ozs./ton	19.24	6.17	41.40	129.60
Copper in per cent.	0.49	2.65	2.20	65.86
Lead in per cent.	31.70	3.65	40.40	2.75

[4] U. S. Pat. 8,756 (1852).

[5] U. S. Pat. 72,032 (1867).

[6] "Metallurgy," p. 449 (1870).

[7] U. S. Pat. 381,301 (1888).

[8] U. S. Pat. 463,184 (1891).

[9] U. S. Pat. 470,970 (1892).

Iles and his associates.[1] During the succeeding sixteen years it was generally accepted that the bag house had reached the limit of its development and could be used only for lead and zinc furnace products—not for copper furnaces or for roasters.[2] Minor mechanical improvements were proposed by Rourke,[3] Hannay,[4] Picher and Boss[5] and others.

The construction of the modern bag house for the Lewis and Bartlett process is so well known that no description of it need be given here.[6] The lead smelter bag house is somewhat different.[7] It consists essentially of two chambers, the lower or dust chamber being twelve to sixteen feet from floor to ceiling, and the upper or bag compartment ranging from thirty to forty-five feet in height. The walls and partitions are usually of brick, properly buttressed or held together by tie rods. The dust chamber or smoke cellar is divided by brick partitions into as many compartments as there are flues leading to the bag house, thus enabling a part of the bag house to be shut down without interfering with the rest of it. The ceiling of the smoke cellar is made of iron or steel plate and is provided with a number of nipples or rings projecting into the bag compartment. From supports near the top of the building bags of cotton or wool are hung, and the lower ends of the bags are tied on to the nipples by means of twine, wire, or hoop bands provided with strap clamps. The older bag houses, designed simply to recover the solids because of their value to the smelter, were built with ventilators along the walls and on the roof; but the more recent ones, intended for the protection of adjacent property as well as for the recovery of values, are provided with stacks that carry the filtered gases two or three hundred feet into the air.

Fans capable of moving 150,000 to 250,000 cubic feet of gas per minute force the flue gases, laden with dust and fume, through a number of large pipes or flues into the smoke cellar and through the bags, and the solids are removed so perfectly that the escaping gases are invisible. The ordinary bag house is provided with 3,000 to 4,500 bags, each bag being about 18 inches in diameter and 30 to 33 feet long. Whereas the earlier bag houses had 750 to 1,100 square feet of filtering surface per ton of charge, modern practice finds 300 to 500 square feet per ton of charge ample. (In zinc filtration a ratio of 150 to 200 square feet of filtering surface per square foot of hearth is customary.)

[1] U. S. Pats. 475,774, 480,834, 484,016, 484,017 (1892).

[2] *Eng. Min. Jour.*, **80**, 55, *et seq.* (1905); Iles, "Lead Smelting" (1902), pp. 2, 170, 203 and 204.

[3] U. S. Pat. 530,553 (1894).

[4] U. S. Pat. 729,492 (1903).

[5] U. S. Pat. 735,904 (1903).

[6] U. S. Pat. 470,970 (1892); Collins, "Metallurgy of Lead" (1899), pp. 72–73; Hofman, "Metallurgy of Lead" (1906), pp. 131–148; *Eng. Min. Jour.*, **83**, 937,1033 (1907).

[7] U. S. Pat. 484,017 (1892); *Eng. Min. Jour.*, **80**, 55 (1905); **83**, 1246 (1907); **84**, 527,575 (1907).

As a filtering medium cotton cloth having 42 to 50 threads to the linear inch and weighing 0.4 to 0.7 ounce per square foot was largely used. The objection to this material was that when used at a temperature approximating 200° F. it became brittle and broke, and if used at temperatures near 100° F. it became weakened by the acid substances in the filtered solids. It was soon learned that bags made of woolen material, like flannel, not only withstood the action of the corrosive agents better than did cotton, but that the woolen fabric retained its elasticity even when used at temperatures of 250° to 270° F. Perhaps this is due to the relatively non-volatile oil contained in the wool, or to the nature of the nitrogenous fiber itself. Modern practice, therefore, is to use the expensive woolen bags rather than the cheaper ones made of cotton. To obtain the benefits of wool, but at a less cost, Iles[1] proposed that a fabric be used in which the warp should be wool and the weft cotton, or vice versa, and Sheedy[2] suggested that the lower section of a bag should be made of flannel (wool) and the upper portion of muslin (cotton). The most recent experience has shown that vegetable fibers should not be used at all. Even linen thread for stitching is unsatisfactory.

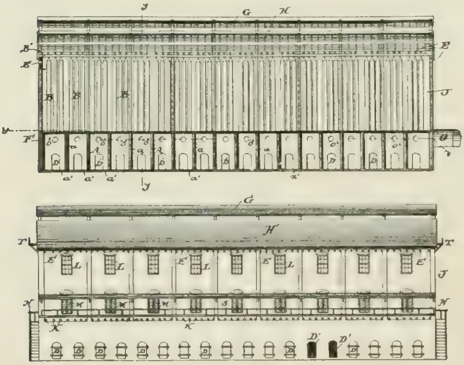
When woolen bags are used a wide range of temperature is permissible. Perhaps 150° to 175° F. is safest, but a minimum of 70° F. and a maximum of 270° F. have been used. The best practice is to so adjust dampers at the furnaces and in the flues as to maintain the temperature as near 160° F. as possible. Under these conditions the material collected in the bag will be dry and filtration can go on rapidly. Lead blast-furnace gases are usually so cool that their treatment in a bag house can take place directly, but the gases from copper furnaces and most roasters ordinarily require cooling. This is effected either by a suitable flue system, which must be as elastic as possible, or by the admission of cold air into the flues with the gases.

Until the investigations of Rhoades and Sprague

[1] U. S. Pat. 485,797 (1892).

[2] U. S. Pat. 480,834 (1892).

(1907–1908) had shown the possibilities of filtering neutralized gases, the bag house was looked upon as not suited for copper furnace and roaster gases (cf. p. 687 above). These experimenters, impressed with the fact that the bag houses at zinc works were sometimes managed in what seemed to them, as lead and copper smeltermen, a very reckless fashion, yet with little apparent ill effects, conducted an extensive series of investigations with a miniature bag house of the type illustrated by Iles,[1] but devised independently by them. A variable speed motor drove a fan that drew gases from a flue and then forced them through a four-inch pipe into a cylindrical dust chamber two by five feet. Upon this cylinder were placed two nipples over which bags were tied. Necessary thermometers, manometers and other instruments were provided, and a house of corrugated iron enclosed the whole apparatus. This experimental bag house was set up at various parts of the flue system of a lead and copper smelter, and the effects of the flue gases with their accompanying solids were determined. During this series of tests neutralizing copper blast furnace and lead roaster gases by means of zinc oxide were tried, and the results were



Iles' bag house.

so satisfactory that now the lead plant is operated under conditions suggested by them for filtering all the smoke from the blast-furnaces, hand roasters working on matte and converter or pot roasters charged with ore. Stacks, which under ordinary conditions emit large volumes of dense smoke, send only colorless gases and no solids into the atmosphere when the bag-filtration plant is used. An observer would judge from the appearance of the stacks that the smelter was not running

Under this system of operation zinc roasting furnaces for the treatment of zinciferous middlings have been erected, and the flue from these furnaces leads directly into the main roaster flue. The middlings, mixed with fuel, are roasted on a grate and the liberated sulphur dioxide and zinc oxide pass into the roaster flue, where the latter oxide neutralizes the corrosive sulphur trioxide that comes from the roasters. Provision is made at the bag house fan for adding ordinary zinc oxide constantly, if need be, by an automatic feeding device.

It would not be economical to use this method, under ordinary conditions, with roasters of the hand or McDougal types, because of the large quantities of sulphur trioxide produced by them; but the treatment of the gases coming from pot or converter roasters presents no difficulties. In these the amount of sulphur trioxide is relatively much less than in the hand or McDougal roaster gases, and zinc oxide neutralization is commercially possible. Were this small amount of sulphur trioxide not to be neutralized, however, the filtering bags would soon be destroyed.[1] Gases from copper blast-furnaces, reverberatories and converters are amenable to treatment under the conditions herein given.

An item of importance in bag house operation is the means adopted for shaking the bags. Originally the method used was to shut off the gas from a set of bags, open the doors in the bag room, and after the noxious gases had escaped shake the bags by hand. This was at best a disagreeable—even dangerous—task and consumed much time. At East Helena a device was provided whereby an attendant could move a lever on the outside of the bag house and have a set of beaters strike against the rows of bags within. The scheme was abandoned, both because the shaking was ineffectual and the wear and tear on bags was great. Rourke[2] attached ropes or wires to rings placed around the centers of bags so that a whole row could be shaken by jerking the end of the rope extending outside the building. The most satisfactory device is one designed by Benedict,[3] in

[1] *Eng. Min. Jour.*, **69**, 647 (1900).

[1] Hand roasters present a double difficulty. Not only is the production of sulphur trioxide large, but the products from coal firing seem to make the bags and their contents liable to spontaneous combustion—a combustion that is not accompanied by flame, but is more like that which one observes in the burning of punk.

[2] U. S. Pat. 530,553 (1894).

[3] Patent pending.

which the bags are suspended from short levers attached to a central shaft. The outer end of this shaft projects beyond the wall and is provided with a larger lever, so that when this lever is moved to and fro the tops of the bags are given a similar motion, and a wavy motion is imparted to the bags as a whole.

The bag house product, collected in the dust chambers or smoke cellar, usually has a black or dark gray color, is quite light (density less than water) and can be handled with difficulty when in its original state. Therefore it is burned. Some oily waste is lighted and thrown upon it, the doors to the dust chambers are opened, and a fan draws the fumes through a flue situated at the back of the chamber and discharges them into the main flue leading to the bag house. Here the fume evolved during the burning is caught in a part of the house that is operating as usual. The material on the floor of the dust chamber burns slowly like punk, gradually sinters to a product resembling soft lava, and loses some of its arsenic and sulphur. The burning continues a number of days, and then the sintered product goes to an arsenic refinery. The white arsenic is volatilized and used as such, and the residual cinder is charged again into the lead blast-furnace. Thus the arsenic, lead, copper and precious metals are recovered.

The labor question has been a serious one in bag house management, and the expenditure of thought and care upon the welfare of the men is imperative. It will not do to put any kind of a laborer in charge of a bag house. The foreman should be at least as able as the charge floor foreman or the head furnaceman, and his helpers should be capable of understanding orders and executing them implicitly. A wash room divided into three parts should be provided. The laborer enters the "clean room," disrobes and places his clothing in sanitary lockers, passes through the "wash room" into the third room and there dresses in heavy underwear, socks, overalls, jumper, cap, gloves and shoes provided by the company. His shift completed he leaves his working clothes where he got them originally, bathes thoroughly from head to foot, using plenty of soap and hot water, and then passes from the wash room to the locker room he entered at first, and there clothes himself. Constant watchfulness on the part of the management is necessary to make sure that the washing is done regularly and thoroughly. Careful attention must be given to the health of the men, and at the first appearance of arsenical or lead poisoning proper antidotes should be administered and the men ought then to be transferred to some other kind of work until recovery is complete. When regulated as here indicated, the same crew of men can work at a bag house for months at a stretch without discomfort or danger.[1]

The objections to the use of a bag house are (1) cost of installation;[2] (2) cost of maintenance; (3) artificial draft must be substituted for natural draft; (4) danger to operatives; and (5) the arsenic saved as a by-product is sometimes disposed of with difficulty.

To offset these disadvantages we must consider (1) the greater recovery of metals; (2) regularity in draft and ventilation; (3) greater safety and less discomfort to the inhabitants of the region surrounding the smelter, and consequently less expense for lawsuits.

University of Utah,
Salt Lake City, Utah.

A COMPARISON OF METHODS FOR THE DETERMINATION OF SULPHUR IN COAL.

By S. W. Parr, W. F. Wheeler and Ruth Berolzheimer.

Received July 10, 1909.

Advantage has been taken of a comparative series of tests on thirty-five coals for the determination of calorific values,[3] to make a further comparison of methods for the determination of sulphur. These methods involve the use of the residues from the bomb calorimeter of the Mahler Atwater type and from the Parr calorimeter, using sodium peroxide as the fusion medium. To these two methods were added the usual Eschka method for the determination of sulphur in coals and the photometric method recently described in the *Journal of the American Chemical Society*.[4]

While this work was in progress, the article by Holliger[5] on the estimation of sulphur in coal appeared, in which the same comparison of methods was made, excepting the photometric process. In that article the fusion method by the use of sodium peroxide is discredited as being subjected to too great personal errors. The result of the work described in this paper goes to show the method

[1] Some idea as to the dangerous nature of the bag house dust may be gained from the fact that it contains from ten to thirty per cent. of arsenic, and from fifteen to fifty per cent. of lead.

[2] A bag house of 4000 bags will cost approximately $150,000.

[3] "A Series of Parallel Determinations with the Mahler and Parr Calorimeters," This Journal, **1**, 673.

[4] *Jour. Am. Chem. Soc.*, **26**, 1139-43.

[5] *Zeit. angew. Chem.*, **22**, 436-49, 493-7.

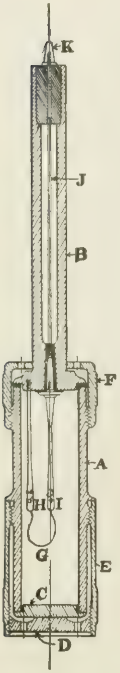


Fig. 1.

to be exceedingly reliable. It is entirely possible that the method of carrying on the fusion may have much to do with this difference of opinion. In the method as pract ced by us the grade of sodium peroxide as especially prepared for the determination of heat values was used and a uniform amount of one gram of potassium chlorate was added to the charge, one-half gram being the amount of coal used. The fusion was carried on in the calorimetric bomb as illustrated in Fig. 1, and was exceedingly uniform and complete so far as the combustion of the material was concerned. The fusion was dissolved and acidified in such a manner as to give approximately 5 cc. of free acid in a volume of 250 or 300 cc. of liquid. Under these conditions the interference of salt or iron was not appreciable. This method has been in constant use and has been subjected to very many tests in this laboratory during the last five or six years and has given at all times evidence of thorough reliability.

In the table presented herewith the gravimetric results obtained by the method of fusion with Na_2O_2 are given in column (1). In column (2), comparison is made with the results obtained by the usual Eschka method modified, however, in that the residue, after burning and dissolving out the soluble sulphates, was found almost without exception to contain sulphur which was not soluble by the usual method of washing with water. This residue, therefore, was treated with acid and a precipitation of the sulphate obtained which was added to the main precipitation from the water solution. Only by this means could a duplication of results be obtained and, when so modified, the results are seen to be in good agreement with the fusion values as obtained under column (1). The differences between the values in columns (1) and (2), using the values in column (1) as a basis, are shown in column (5).

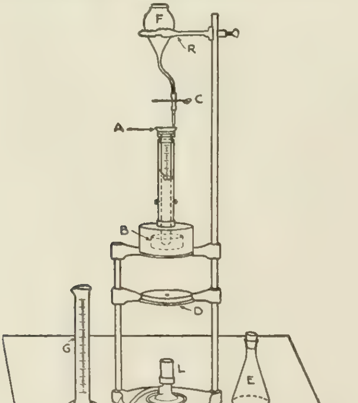


Fig. 2.

Comparison of Methods for the Determination of Sulphur

Lab. No.	Table No.	Method No. 1, Na_2O_2 fusion. Gravimetric. (1) Per ct.	Method No. 2, Eschka. Gravimetric. (2) Per ct.	Method No. 3, washings from Mahler bomb. Gravimetric. (3) Per ct.	Method No. 4, Na_2O_2 fusion. Photometric. (4) Per ct.	Method 1–2, diff. (5) Per ct.	Method 1–3, diff. (6) Per ct.	Method 1–4, diff. (7) Per ct.
2111	1	1.82	1.72	1.65	1.71	—0.10	—0.17	—0.11
2112	2	1.26	1.21	0.90	1.08	—0.05	—0.36	—0.18
2113	3	0.92	0.81	0.82	0.63	-0.11	-0.10	—0.29
2114	4	4.41	4.29	4.05	4.48	—0.12	-0.36	+0.07
2115	5	1.79	1.81	1.77	1.75	+0.02	—0.02	—0.04
2116	6	3.83	3.78	3.60	3.68	—0.05	-0.23	—0.15
2117	7	3.48	3.42[1]	3.21	3.32	0.06	—0.27	—0.16
2118	8	3.76	3.84[1]	3.62	3.68	+0.08	-0.14	—0.08
2119	9	4.80	4.81[1]	4.31	4.80	+0.01	—0.49	±0.00
2120	10	3.20	3.13	2.89	3.00	—0.07	—0.31	—0.20
2121	11	5.57	5.81[1]	5.25	5.60	+0.24	—0.32	+0.03
2122	12	2.68	2.62[1]	2.48	2.54	—0.06	—0.20	—0.14
2123	13	3.44	3.31[1]	3.20	3.34	—0.13	—0.24	—0.10
2124	14	3.09	3.22	2.85	3.14	+0.13	—0.24	+0.05
2125	15	0.93	0.89	0.76	0.66	—0.04	—0.17	—0.27
2126	16	0.82	0.81	0.72	0.62	—0.01	0.10	—0.20
2127	17	0.97	1.02	0.94	0.72	+0.05	—0.03	—0.25
2128	18	1.12	1.14	1.09	0.82	+0.02	—0.03	—0.30
2129	19	0.96	0.95	0.93	0.85	0.01	—0.03	—0.11
2130	20	1.00	0.92	1.01	0.76	—0.08	+0.01	—0.24
2131	21	0.72	0.62	0.70	0.51	—0.10	—0.02	—0.21
2132	22	0.70	0.63	0.64	0.53	—0.07	—0.06	—0.16
2133	23	1.41	1.39	1.36	1.32	—0.02	0.05	—0.09
2134	24	1.26	1.16	1.20	1.16	—0.10	—0.06	—0.10
2135	25	1.63	1.53	1.50	1.73	-0.10	-0.13	+0.10
2136	26	0.52	0.50	0.54	0.31	0.02	+0.02	0.21
2137	27	1.31	1.23	1.21	1.15	—0.08	—0.10	—0.16
2138	28	2.64	2.64	2.50	2.50	±0.00	—0.14	—0.14
2139	29	0.80	0.77	0.64	0.70	—0.03	—0.16	—0.10
2140	30	1.20	1.23	0.95	1.16	+0.03	—0.25	—0.04
2141	31	0.64	0.67	0.61	0.52	+0.03	—0.03	—0.12
2142	32	1.25	1.29	1.22	1.18	+0.04	-0.03	—0.07
2180	33	5.07	4.97	4.62	4.95	—0.10	—0.45	-0.12
2193	34	2.54	2.58	2.40	2.58	+0.04	—0.14	+0.04
2194	35	3.01	2.99	2.80	3.16	—0.02	-0.21	+0.15
Average		2.13	2.11	1.97	2.02	0.02	-0.16	-0.11

In column (3) are listed the values obtained in

[1] The magnesium oxide and carbonates and residue insoluble in water were not dissolved in hydrochloric acid as they were in all other determinations by the Eschka method.

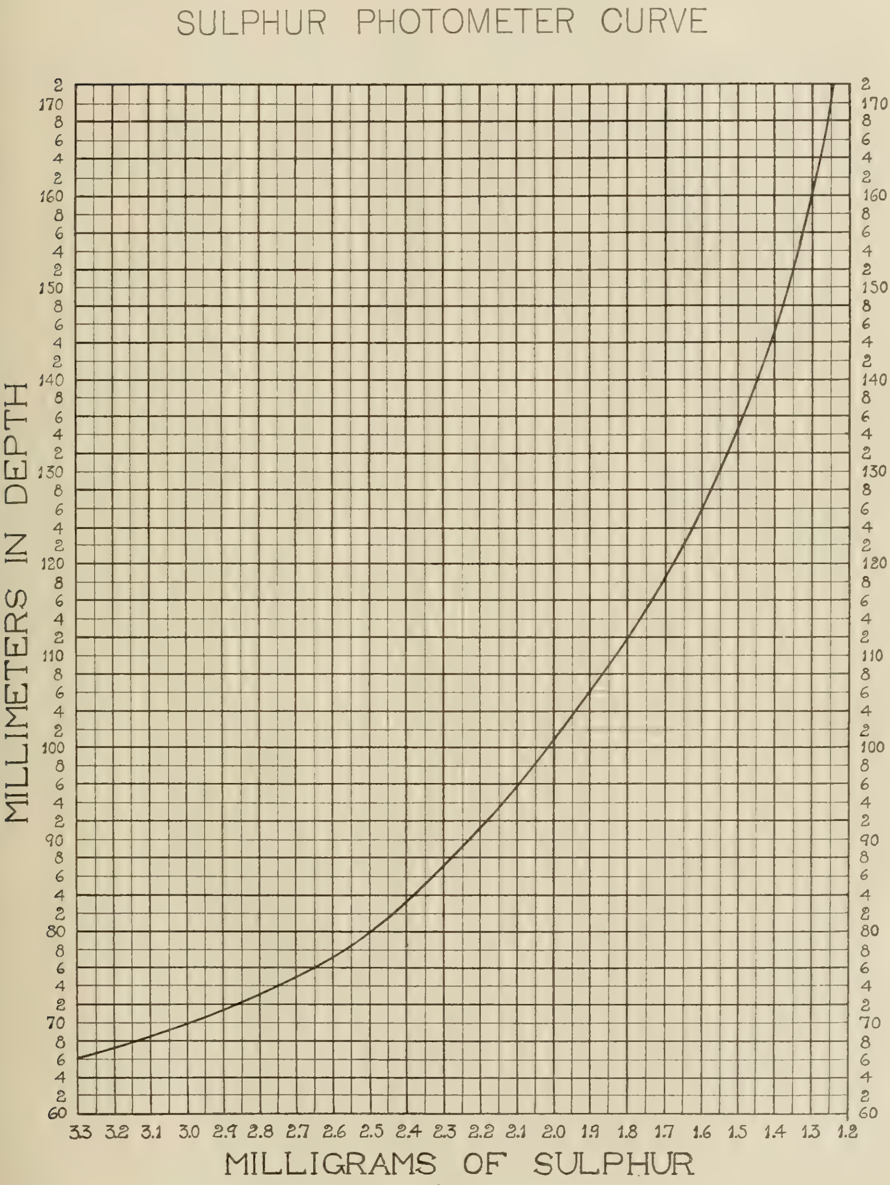

SULPHUR PHOTOMETER CURVE
MILLIMETERS IN DEPTH
MILLIGRAMS OF SULPHUR
3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
60 70 80 90 100 110 120 130 140 150 160 170

Fig. 3.

the washings from the Mahler-Atwater bomb. These values are not in such close agreement to the values in column (1) and it may be argued in explanation that the sulphur thus obtained represents the combustible sulphur. The values are almost without exception lower. The differences between the values in columns (1) and (3) are shown in column (6).

In column (4) the values have been obtained by means of the photometer as illustrated in Fig. 2.

The standard light (L) is made to read through the precipitated material in the graduated tube (A), the lower end of which is submerged in the cup (B). By this means a lens effect is secured and the end point is made very sharp and distinct. Aside from the improved form of apparatus shown in Fig. 2, the chief modification of the process made use of in the present series was the use of a small amount of oxalic acid in conjunction with barium chloride, which precipitates the barium sulphate in a very nearly colloidal condition, at least it does not settle readily and is uniform in its action towards the transmission of light. The curve as shown in Fig. 3 affords a ready means for determining the weight of sulphur in milligrams to correspond with the depth of the solution in millimeters.

It cannot be expected that such a method will have the same degree of accuracy that should accompany a gravimetric method, but for technical purposes it is admirably adapted as a quick and ready process for determining the sulphur in the fusion residues from calorimetric determinations by the use of sodium peroxide. Comparison as between this method and the gravimetric fusion method of column (1) is shown in column (7).

It may be well to call attention to one advantage in this series over the tests made by Holliger, in that three times the number of coals are tested, sufficient to bring out any variations that inhere in the various processes. It should be borne in mind that the fusion method No. 1 yields the total sulphur, while the tendency of method No. 3 is to yield the burnable sulphur rather than the total sulphur. If this latter distinction were sharply drawn, that method would have an advantage. On the other hand, method No. 1 has the advantage of certainty of oxidation when conducted as herein described, and there can be no question about the completeness of the process. It is, therefore, given preference in the table and the others are arranged in the order of what seems to be their respective merits. The coals are widely distributed; their source, as may be seen by reference to the article on calorimetric values above referred to, is from Pennsylvania, West Virginia, Kentucky, Alabama, Maryland, Kansas, Indiana and Illinois.

UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS.

STUDIES IN THE USES OF FINELY DIVIDED SILICA.[1]

By S. W. PARR, T. R. ERNEST AND W. S. WILLIAMS.

Received August 7, 1909.

The extensive deposits of finely divided silica found in Southern Illinois have furnished, in very large measure, the incentive for some work in the Department of Applied Chemistry of the University of Illinois during the last two years. This work has consisted mostly of experiments on compounds such as are formed at steam temperatures between this material and lime.

It was found that bricks made in this way possessed, after steaming, good texture and strength. This suggested a series of experiments to determine the best ratio of lime to silica. Then the idea of making briquettes by moulding without pressure suggested itself, and with it came the question as to the best conditions for maximum strength. In the first case the briquettes were made by compression and tested for crushing strength while in the second a cement briquette mould was used and briquettes were tested for tensile strength. In the first case the best lime silica ratio was found to be one mol. of lime to one of silica, while in the latter the best results were attained when 20 per cent. of lime was used with 80 per cent. of amorphous silica as is shown by the following tables:

TABLE I.

Data.........Steam pressure 105 lbs. per sq. in.
Time exposed to steam, 10 hrs.

Per cent. lime.	Per cent. silica.	Tensile strength, lbs. per sq. in.
10	90	135
20	80	265
30	70	202
40	60	189
50	50	150

TABLE II.

Data:.......Steam pressure 150 lbs. per sq. in.
Time exposed, 10 hrs.

Per cent. lime.	Per cent. silica.	Tensile strength, lbs. per sq. in.
10	90	134
20	80	278
30	70	204
40	60	169
50	50	148

[1] An examination of this material made some years ago showed it to be of chalky appearance sometimes stained by iron. It consists of

TABLE III.

Data:.........Steam pressure 50 lbs. per sq. in.
Time exposed, 10 hrs.

Per cent. lime.	Per cent. silica.	Tensile strength, lbs. per sq. in.
10	90	102
20	80	182
30	70	116
40	60	94
50	50	71

An attempt was made to ascertain whether or not pressure was needed to bring about this reaction, or whether it was caused by the heat of saturated steam together with the moisture. To do this, briquettes were made in the usual way and placed in a chamber that could be heated from without to a temperature corresponding to that of saturated steam at 150 pounds pressure. Steam was then generated in a flask and superheated to the temperature of the chamber after which it was passed over the briquettes. The time of exposure varied from ten to forty-eight hours, but in no case was there any noticeable reaction. From this it was concluded that pressure as well as heat and moisture is required to bring about the reaction.

The effect of heat on these briquettes is rather interesting, as is shown by the following table:

TABLE IV.

Test number.	Drawn at temperature, ° C.	Tensile strength, lbs. per sq. in.
0	20	278
1	300	45
2	400	0
3	500	101
4	600	131
5	700	124
6	750	27
7	800	71
8	850	186
9	1190	260
10	1390	263

As this behavior is not what one would expect, the work was repeated several times with substantially the same results.

After finding the best proportion in which to mix the lime and silica to give the best tensile strength, experiments were made in which other substances were introduced into the briquette. Magnesia was found to work about the same as lime. It was found that the introduction of about four parts of sharp sand into a mixture of equal parts of lime and silica (one part) gave a product with much higher tensile strength than when no sand was used.

minute particles of silica, from 50 mm. to 0.2 mm. in diameter, of crystalline structure, transparent and irregular in shape, loosely cemented together by a small amount of clay. An analysis showed: Moisture, 0.15%; silica, 98.00%, magnesium oxide, 0.20%; aluminium oxide, 1.21%; undetermined, 0.44%.—ED.

The effect of the addition of fibrous material was next studied, and the first to be tried was slag wool. The addition of varying per cents. of this material did not materially affect the strength until enough was added to dilute the original material so much that it resulted in a weakening of the bond. There appeared to be no union between the fiber and lime. A cheap grade of asbestos was tried next. The results of the tests are shown in the following table:

TABLE V.

Data:...........Steam pressure, 150 lbs. per sq. in.
Time of exposure, 10 hrs.

Per cent. asbestos.	Tensile strength, lbs. per sq. in.	Increase in tensile strength.
3	285	7
4	297	19
5	300	22
10	343	65
12	377	100
14	302	24
20	242	—36
40	173	—105

From the table it will be observed that the tensile strength rises with the addition of asbestos until 12 per cent. is added, when the drop is sudden. It will be noticed, too, that the strength of the material may be increased very materially by the addition of this fiber.

The effect of the addition of colloids was next studied. To the regular mixture of lime and silica (20 per cent. CaO to 80 per cent. SiO_2), varying per cents. of sodium silicate and of Portland cement were added and the briquettes made and tested in the usual way. The results showed a decrease in the strength in every case, which in the case of the sodium silicate was about 66 per cent. of the original strength when only 5 per cent. was added.

Mixtures of lime and silica in the proportions for best tensile strength were found to possess good plasticity, this property being possessed in about the same degree as in the case of Georgia kaolin. This discovery led to an attempt to make a vase of this material. The regular mixture of lime and silica was used, enough water being added to give the best plasticity, and the vase moulded by hand in a plaster of Paris mould. When dry, the vase could be removed and the joints finished. When hardened by steam it had, when struck with a pencil, the true hard ring of vitrified clay biscuit. The material easily took the form and markings of the mould; there was no shrinkage that was noticeable and the color was a good clear white. No attempt was made to prepare a vase by making the mixture up with enough water so that it could

be poured into a mould in the form of a slip, but there can be little doubt as to the possibility of making ware in this way. Small trials were also made by jiggering, which were very successful.

These experiments suggest the possibility of using this process for making architectural building material to be used in a way similar to terra cotta. The manufacturer of terra cotta has many obstacles to overcome in the process of burning. His ware may warp or be of the wrong color; it may shrink excessively or be defective in some other way. The manufacture of artificial stone that might be used similarly to terra cotta might be made, it seems, very advantageously by this process.

University of Illinois,
Urbana, Ill.

CYANIDATION OF SILVER MINERALS.

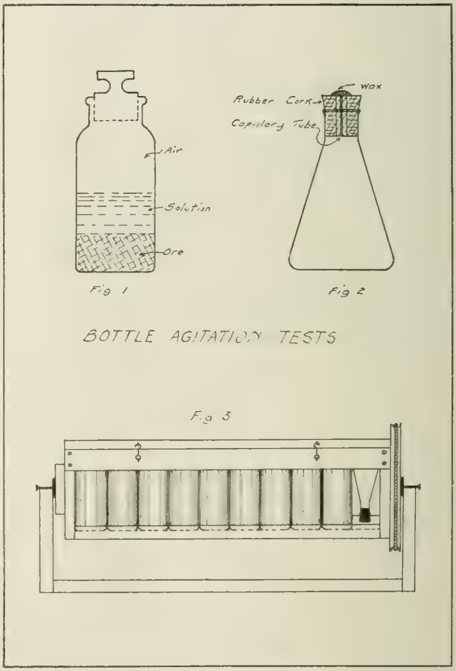
By Theo P. Holt.

Received July 17, 1909.

This paper embodies some results of an investigation carried out during the past year, under the Wall Research Fellowship at the Utah State School of Mines. From a mechanical standpoint, the adaptation of the cyanide process from gold to silver ores has been very satisfactorily worked out, but chemically the development has been slow, and to quote a well-known writer, "It is difficult to differentiate between fact and fancy in dealing with the available evidence on the subject." It was with the hope of clearing up some of these mooted questions that this investigation was undertaken.

The experiments, which are represented in graphic form, were conducted in 8-oz. bottles. Ten of these were clamped in a suitable frame which was rotated by a small water motor. The speed of the motor was so regulated that the contents of the bottle would fall from one end to the other during each half revolution. The bottles were only partly filled so that an excess of oxygen was assured. The conditions favoring extraction are as good as obtained with air agitation, while variations due to gases present in the air, evaporation, etc., are largely eliminated. Thus it is possible to estimate closely the consumption of cyanide due to the minerals present in the ore, and determine the amount of any metal dissolved from solution assays.

The value of experimental tables showing variations in results, secured by changes in treatment, is largely determined by the accuracy of our knowledge of the active agents at work in the test. In case several unknown factors enter into an experiment, we simply get a mass effect, and are unable to judge with safety the action of each agent. For this reason the significance of a set of tests on any particular ore is limited. The results on another ore of similar chemical composition may be quite different, due to mineralogical and physical differences. Thus it has been aptly said "that each ore is a problem in itself."



In consideration of the above facts I have made most of my experiments on chemical compounds and artificial ores of known mineralogical composition. Active agents, met with in cyanide practice, have been added singly. One example will serve to illustrate the general procedure. About 1.6 gms. of a crystallized specimen of pyrargyrite (Ag_3SbS_3) were crushed with a few grams of quartz sand in a porcelain mortar, to pass a 100-mesh screen. This was then mixed with 550 grams of quartz sand, which had been ground on a stone bucking board to avoid the introduction of iron. After adding 1.6 gms. of lime the sample was thor-

oughly mixed and quartered. The method of preparation favors a large number of mineral particles approaching the maximum-sized grain that will pass the screen. This will in a measure

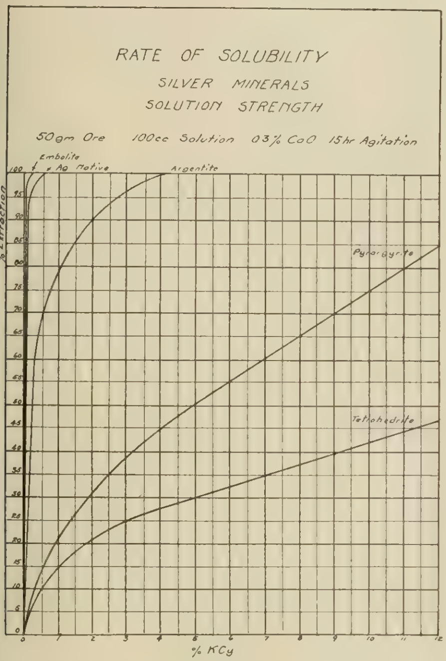


Fig. 4.

offset the fact that none of the mineral is encased in the gangue. No doubt the surface of mineral exposed to the action of the cyanide solution is much less than obtains in modern slime practice.

All solutions were titrated with a standard silver nitrate solution. In cases where the silver mineral is the only cyanicide present, it is possible to calculate quite closely the extraction secured by the amount of KCy consumed. The per cent. of silver dissolved was computed in all cases from fire assays. The original ore was assayed in duplicate, and the result checked by assays on both the tail and the solution.

Compounds, other than potassium and sodium cyanide, used to assist in the solution of silver, are termed "chemical salts" by cyanide mill men. In treating ores containing their silver chiefly as argentite, these are of great practical importance. The degree to which they are capable of influencing the amount of silver dissolved, may be appreciated when we inspect the graphic results of a few tests. Take the line for argentite for an example. A 0.5 per cent. KCy solution dissolves 38 per cent. in 17 hours. The addition of 0.3 per cent. lime brings this up to 58 per cent. By making the solution strongly alkaline with KOH almost 97 per cent. of the silver is dissolved in the same time. A small amount of litharge is about equally effective.

To explain this action requires reference to the primary equation for the solution of silver sulphide:

$$Ag_2S + 4KCy \leftrightarrows 2KAgCy_2 + K_2S$$

This reaction proceeds only to a slight extent before equilibrium is established between the S^{--} ions, the Ag^{+} ions and the undissociated Ag_2S. Litharge (PbO), although it enters the solution as a plumbite, still dissociates a sufficient number of lead ions to effectively remove the S^{--} ions

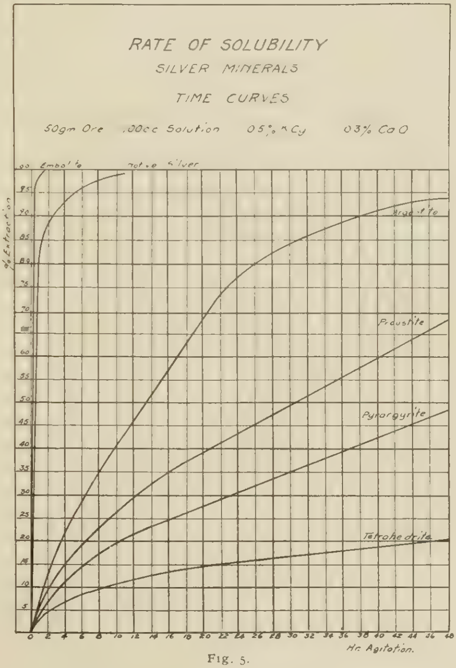


Fig. 5.

as insoluble PbS. Thus the presence of the lead salt prevents the equilibrium indicated above being established and the solution of silver sulphide proceeds. Any metal whose sulphide is but slightly

soluble in cyanide solution will produce a similar effect.

The increased extraction observed on adding potassium hydroxide to the solution, is also in

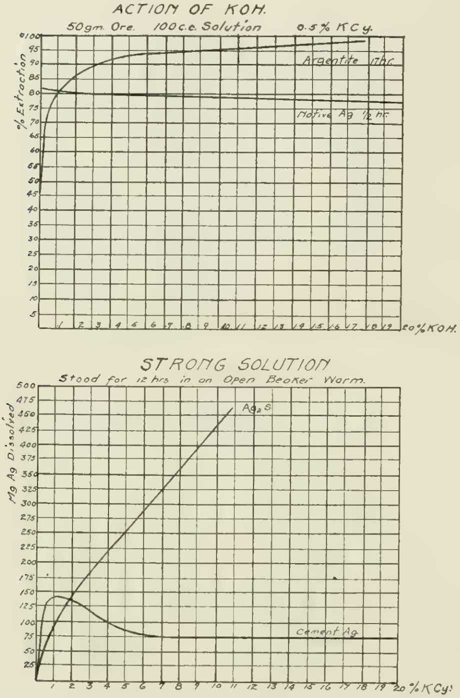


Fig. 6

accordance with the mass law. In this case we have

$$(K_2S)k = (2K^+) \times (S^{--}).$$

Upon adding a highly dissociated base as KOH, we greatly increase the number of K ions, and hence the product on the right of the equation. To establish ionic equilibrium some of the K ions must unite with S ions to form undissociated K_2S and thus effectively removing S ions from the solution. Theoretically any highly ionized compound capable of forming a slightly dissociated compound with sulphur, will increase the solubility of silver sulphide.

From a practical standpoint the use of some metal to precipitate the sulphur in an insoluble form is much to be preferred, as any other method results in the fouling of the solution by the accumulation of sulphur compounds. Lead acetate is the salt most extensively used in practice for the precipitation of soluble sulphides. Litharge has been substituted in one or two instances to advantage. It is less expensive both on account of the higher lead content, and less cost per pound. Litharge has the further advantage that a slight excess does not seriously affect the results, as is the case with lead acetate.

Mercury compounds are also effective precipitants for soluble sulphides, but are more expensive than lead salts. Hobson[1] experienced very beneficial results on a certain Mexican silver ore by the addition of mercurous chloride to an alkaline cyanide solution. He attributes his success to the property of "mercurous potassic cyanide" to dissolve argentite, pyrargyrite, stephanite and

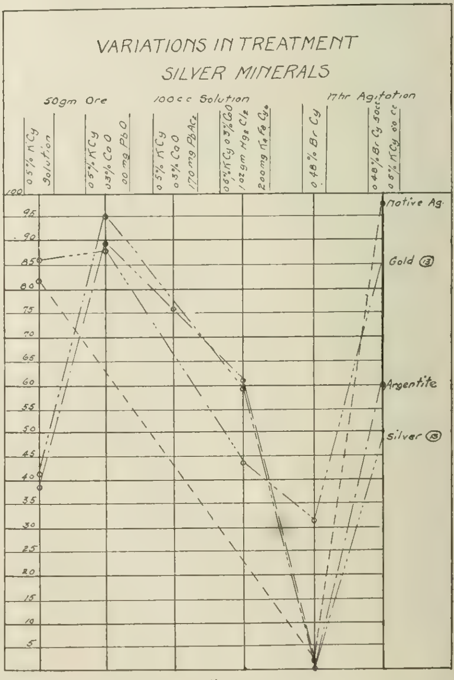


Fig. 7.

proustite. It has been pointed out later by both Hunt[2] and Sharwood[3] that the compound "mercurous potassic cyanide" does not exist. The

[1] *Min. and Sci. Press*, Aug. 8, 1908.
[2] *Ibid.*, Aug. 29, 1908.
[3] *Ibid.*, Sept. 26, 1908.

formation and action of mercury compounds are discussed rather fully in these two articles. I have tested out the chemical combination given by Hobson on several of the silver minerals, and

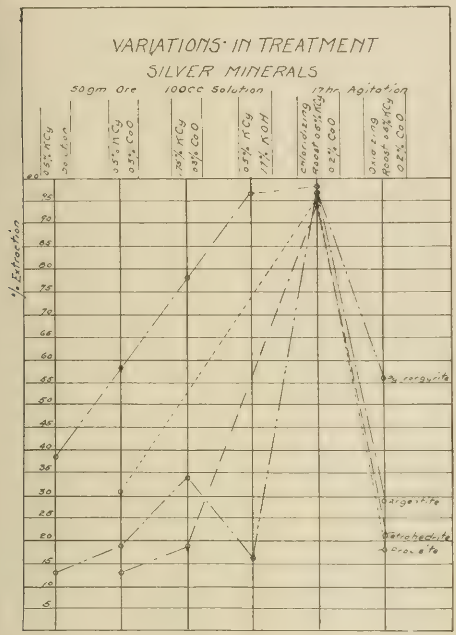


Fig. 8.

with the exception of argentite, have experienced no beneficial results. The general conclusion would seem to be that the mercury is effective chiefly by virtue of its ability to remove soluble sulphides.

Bromocyanide is an energetic oxidizer, and its property of dissolving gold is well known. At the present time it is being successfully applied to gold ores which cannot be treated by plain cyanide. Some statements have been made regarding the adaptation of bromocyanide to silver ores. I find that in the absence of free cyanide it is not a solvent for the silver minerals. At any rate its solvent power is so slight as to be of no value. The addition of a limited quantity of bromocyanide to a cyanide solution is quite effective in increasing the extraction, in some cases, due to its oxidizing power.

A chloridizing roast of silver sulphide ores is an essential preliminary to successful treatment by the old processes. With cyanidation it has been found possible to treat successfully a great many such ores without roasting, and hence one of the strong points favoring the cyanide process. It is likely, however, that many cases exist where roasting could be employed to advantage. In fact in some cases it seems the only means of securing a satisfactory extraction.

A number of the "ore samples" were given a one-hour roast in an open muffle at a dull red heat. It is evident from the graphs that a chloridizing roast is about equally effective in all cases, the silver being converted into a chloride which is readily dissolved. For an oxidizing roast one hour is too brief a period to change materially the state of the silver minerals.

There are many interesting points suggested by the tabulations and graphs that are not mentioned in this discussion. For instance in the "variations in treatment," it is remarkable how closely the silver of ore "13" follows the line for argentite.

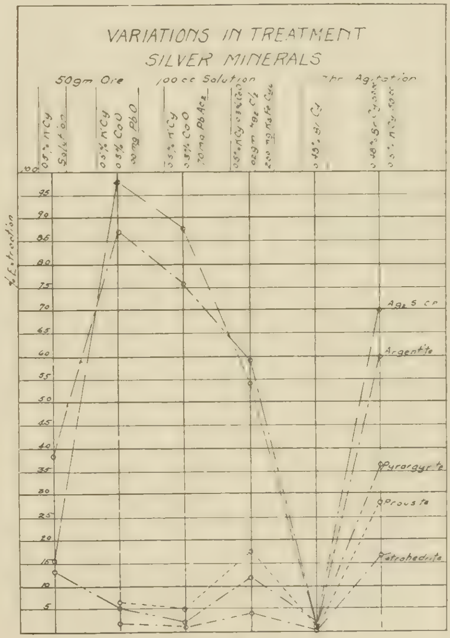


Fig. 9.

It was proven by independent tests that the silver present in this ore is practically all present in the form of argentite.

In conclusion it may be well to summarize some

of the more important points regarding the chemistry of the cyanide process as applied to silver ores.

Each silver mineral presents its own peculiar difficulties. The fundamental laws of chemistry explain in a remarkable way many of the reactions otherwise obscure. Results obtained from experiments on ores are often misleading due to their complex nature. It is therefore advisable to work on artificial ores of known mineralogical composition, before making generalizations regarding the several minerals.

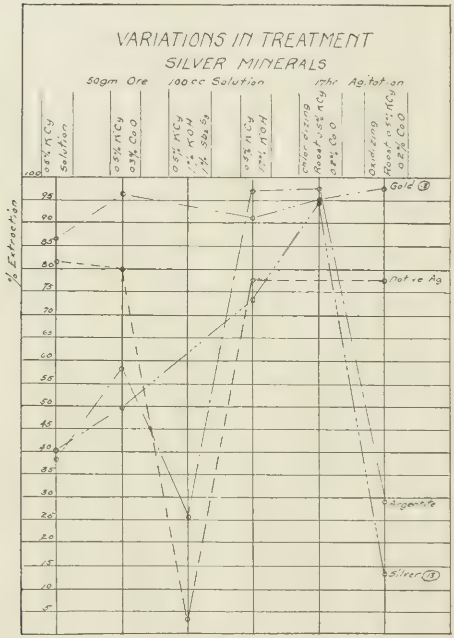


Fig 10.

The halogen compounds of silver are the most soluble form in which it occurs, and no oxygen is required for their solution in potassium cyanide. Native silver is next in order of solubility in an aerated solution, and it dissolves in accordance with Ellsner's equation.

The silver sulphide, argentite, requires the removal of soluble sulphides to insure good extraction. Lead salts are applied for this purpose, and litharge, though less used, presents decided advantages over lead acetate.

Mercury compounds are effective by virtue of their ability to form insoluble sulphides, and not by their property to dissolve the "rebellious minerals."

Oxygen or an oxidizer is essential to the continued solution of silver sulphide in cyanide, even in the presence of lead salts.

The presence of lead or mercury compounds decrease the solubility of the complex antimony and arsenic silver minerals, in a cyanide solution.

Bromocyanide is not a solvent for the silver minerals. In the presence of free cyanide it may give beneficial results by virtue of its power as an oxidizer.

A chloridizing roast is about equally effective on all the silver minerals, and subsequent treatment by cyanidation will give good extraction.

The problem of interfering minerals is more serious in the cyanidation of silver than it is for gold. This is due to the stronger solutions used, and the greater chemical activity of silver.

State School of Mines, University of Utah,
Salt Lake City, Utah.

THE ESTIMATION OF PYRIDINE IN AQUA AMMONIA.

By A. C. Houghton.

Received July 17, 1909.

Owing to the increasing use of anhydrous ammonia for refrigerating purposes, the manufacturer of aqua ammonia has been called upon to furnish a very pure product. The presence of pyridine has proved especially troublesome to the maker of anhydrous ammonia, as, being basic in character, it escapes the purifying trains that serve to hold back the impurities of acid character, such as carbon dioxide and sulphuretted hydrogen, and goes over with the ammonia gas to the compressor, where it separates out before the ammonia is liquefied, and causes trouble by filling up the traps that serve to catch any moisture remaining in the gas, finally going over to the anhydrous ammonia. Even an aqua ammonia testing as low as 0.2 gram per liter in pyridine will cause considerable trouble, as in working off a carload of 25 cubic meters, all the pyridine present, amounting to 5,000 grams, eventually finds its way to the compressors. The elimination of pyridine from aqua ammonia presents no particular difficulty, but it is important to have an accurate and reliable method of estimating small amounts of pyridine in the presence of a large excess of ammonia, in order that the liquors in the different

stages of manufacture may be followed, and the amount of pyridine present controlled. As none of the methods given in the literature are sufficiently accurate or reliable for this purpose, the following work was undertaken in the hope of finding a satisfactory means of estimation.

The property that pyridine has of forming a double compound with mercuric chloride may be made the basis of a very satisfactory determination. If an excess of mercuric chloride is added to a mixture of pyridine and ammonia, the double compound $C_5H_5N.HgCl_2$ is formed and the ammonia reacts with mercuric chloride according to the equation

$$2HgCl_2 + 4NH_4OH = NHg_2Cl + 3NH_4Cl + 4H_2O.$$

The precipitate consisting of NHg_2Cl and $C_5H_5N.HgCl_2$ is filtered off, and on thoroughly washing with water at about 60° C., the pyridine compound, which is soluble in hot water, is dissolved out. The filtrate and washings then contain ammonium chloride, the double compound of pyridine with mercuric chloride, and excess of mercuric chloride, and on long-continued boiling the pyridine compound is completely dissociated into pyridine and mercuric chloride, pyridine passes over as the only free base, and may be titrated with standard acid.[1] The distillate, however, always shows a test for ammonia with Nessler solution, owing, no doubt, to the slight dissociation of ammonium chloride, and further, the method requires considerably more time and more careful work than the one now to be described.

While working on this problem of the estimation of pyridine, Mr. Carl Sundstrom, of our Detroit laboratory, called my attention to the sodium hypobromite reaction with ammonia. As is well known, sodium hypobromite oxidizes ammonia according to the equation

$$2NH_3 + 3NaOBr = 3NaBr + N_2 + 3H_2O.$$

It was found to have no action on pyridine, however, as would be expected from the fact that there is no oxidizable hydrogen combined with the nitrogen atom in pyridine, and as the following experiment shows.

Varying amounts of a tenth-normal solution of pyridine were added to 50 cc. of a tenth-normal solution of ammonium chloride. An excess of sodium hypobromite solution was then added, the flask shaken until no more gas was evolved, and after adding a little caustic soda, the liquor distilled for pyridine, and the distillate titrated with tenth-normal acid. The following results were obtained:

Grams pyridine taken.	Grams pyridine found.
0.000	0.0002
0.006	0.008
0.013	0.014
0.025	0.025
0.032	0.027
0.038	0.039
0.044	0.042
0.051	0.047
0.057	0.057
0.063	0.063

In testing aqua ammonia the method of procedure is as follows:

100 cc. of aqua ammonia are put into a liter flask with about 150 cc. of distilled water, a few drops of methyl orange indicator added, and the liquor carefully neutralized with dilute sulphuric acid (1–3) until just acid, the flask being kept cool under the tap to prevent escape of pyridine. The liquor is now brought to the neutral point with normal alkali, made alkaline with 5 cc. of normal caustic soda, and distilled into 10 cc. of normal acid with a little water in a quart flask, twenty minutes' boiling being sufficient. Pyridine being a weaker base than ammonia is liberated first by the caustic soda, and the distillate contains all the pyridine present in the 100 cc. of aqua, and some ammonia. With aquas containing large amounts of pyridine, it would, of course, be necessary to make the neutralized aqua alkaline with more than 5 cc. of normal caustic soda, but in this case it would be better to start with a smaller amount than 100 cc. The ammonia in the well-cooled distillate is now destroyed by adding 100 cc. of sodium hypobromite solution (made by dissolving 100 grams caustic soda in 1000 cc. of distilled water, cooling, and adding 25 cc. of bromine), the liquor is shaken for a few minutes until no more gas is evolved, and the pyridine distilled over into an excess of tenth-normal acid, a Kjeldahl distilling bulb being used to prevent any mechanical carrying over of caustic soda. The excess of acid in the distillate is titrated back with tenth-normal caustic, using methyl orange indicator. 1 cc. tenth-normal acid is equivalent to 0.0079 gram pyridine. When only small amounts of pyridine are present, the end point with methyl orange indicator is quite sharp, and the titration can easily be made to within 0.1 cc. of tenth-normal

[1] Since the above work was done, I have found that Kinzel in the *Pharmaceutische Centralhalle* (1890), **31**, 239, has already worked out a method for the quantitative estimation of pyridine in ammonia based on this same property of the easy dissociation of the double compound of pyridine with mercuric chloride.

acid, but with larger amounts of pyridine the end point is more or less indefinite, owing to the acid character of pyridine salts. Even in this case, however, it is possible to get the end point within 0.5 cc. of tenth-normal acid, and this does not introduce an error of more than 0.04 gram per liter pyridine.

To check up the method finally, known amounts of pyridine were added to aqua ammonia absolutely free from pyridine. As ordinary chemically pure ammonia always contains pyridine, it was necessary to prepare an aqua ammonia entirely pyridine-free, which was done by heating Merck's c. p. ammonium chloride with calcium hydroxide, neglecting the first portions of ammonia given off, and then absorbing the evolved gas in well-cooled distilled water. The aqua thus prepared contained 24% NH_3, and when carefully neutralized with acid gave absolutely no odor. To this pure ammonia was added weighed amounts of chemically pure pyridine, which had been dried over solid caustic potash and carefully re-fractioned, and the estimation carried through exactly as described above. The following results were obtained, which leave nothing to be desired in the way of accuracy.

Grams per liter pyridine present.	Grams per liter pyridine found.
0.00	0.008
0.05	0.05
0.10	0.10
0.15	0.14
0.20	0.21
0.40	0.38
0.60	0.57
0.80	0.81
1.00	1.06

Duplicates of some of the above tests were also run through, but instead of adding methyl orange and titrating the final distillate, it was tested with Nessler solution. In no case, however, was even a slight coloration obtained, showing that the ammonia had been completely destroyed, so that the only alkaline body that passes over in the final distillation is pyridine and its homologues.

Since the above method was worked out, it has been slightly modified by Dr. D. A. Morton, of this laboratory, who found that it was possible to carry out the estimation with only one distillation, with no loss in accuracy. After the aqua is neutralized and the 5 cc. of normal caustic added, it is distilled through hypobromite solution. An ordinary one-pint sample bottle is fitted with a two-hole rubber stopper, through one hole of which passes the delivery tube from the distillation flask, reaching nearly to the bottom of the bottle, and through the other a Kjeldahl bulb, connected, of course, by rubber tubing with the flask containing tenth-normal acid to absorb the pyridine. 100 cc. of sodium hypobromite solution are placed in the bottle, the stopper inserted tightly, and the distillation commenced. The bottle is not cooled, and the steam from the distillation soon heats the contents to boiling, the ammonia coming over being destroyed, and the pyridine passes over to the receiver. With this modification a single test may easily be made in half an hour.

The method described above has been in use in this laboratory for several years, and has proved itself very satisfactory and reliable.

LABORATORY OF THE SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

FLOUR BLEACHING, ITS RELATION TO BREAD PRODUCTION AND NUTRITION.

By JOHN A WESENER AND GEORGE L. TELLER

Received July 29, 1909.

This question has received much attention of late, both in this country and in Europe, in its relation to economics, bread production and nutrition. It has also found a prominent place in the courts, and recent rulings by the Department of Agriculture indicate that it will receive still further attention in this connection. The questions involved are so imperfectly understood, not alone by laymen but also by most scientists, that they should be clearly outlined, and it is the province of this paper to bring this data before the reader in an accurate and concise manner. Not only is the interest of the general public at stake, but there is also involved the rights of the manufacturer, as relating not only to the economics from his view point, but also as these economics may have a direct bearing upon the consumer.

From an early date in the production of wheat flour the bleaching of the color has been practiced by millers before putting their product upon the market. Up to within the last decade the method employed was to store the flour for a period of several months whereby the more or less marked yellow color of the flour was removed.

Not many years ago, a Frenchman, Frichot,[1] discovered that the gas produced by discharges of electricity through air were capable of whitening the flour. He did not explain properly the cause of this whitening, but attributed it to the production of ozone (which it is now known does not readily bleach flour).[2] It remained for two Eng-

lishmen by the name of Andrews[3] to discover that the bleaching was brought about by the action of certain oxides of nitrogen which are produced when nitric acid is brought in contact with a reducing agent such as ferrous sulphate. Numerous processes have been brought forth for applying this principle to practical bleaching of flour in the mill. The process, which has up to the present time gained the greatest ascendency in this country, is what is known as the Alsop process, where air is pumped through a chamber in which a flaming electric arc is discharging. It can readily be shown that the air discharged from the pump contains small quantities of oxides of nitrogen. In more recent times the use of nitrosyl chloride has been introduced into the art of flour bleaching and possesses advantages over the oxides of nitrogen in the character of the bleach which it produces as well as in the simplicity of application to the flour. This gas can readily be liquefied and bought in small bulk for convenience of transportation and storage. The pressure is ideal for the purpose, being at normal temperature from 15 to 20 pounds to the square inch, and is an important point, as it materially aids in the methods of applying the gas to the flour.

Color is probably one of the most important factors entering into foods, because it plays an important rôle in the mind of the consumer, bringing in a physiological factor which not only affects the palatableness of the food, but also the health of the consumer. The United States government took advantage of that factor in passing the Oleomargarine Act, imposing a tax of 10 cents a pound on this product when colored.

In the earlier milling process where the wheat was ground between stones and the resulting meal separated through a simple bolting device, the flour was often improved by the method of storing which was called ageing, and which ageing process, while maturing the gluten to some extent, was clargely used for the purpose of whitening the flour. By the introduction of the roller process, which became general only within the last half century and only after considerable opposition, a flour was produced which was much whiter in color than was generally produced by the use of millstones. Some consumers of this flour complained that while it was whiter in color it would not make good bread, which was probably due largely to their prejudice against the new flour, commonly known as patent flour. In spite of this prejudice, the desire for the new flour became general and every mill was eventually compelled either to go out of business or adopt this system.

In the roller process of milling the wheat is first run lightly through a pair of rolls so that it is broken into fragments, and care is taken that the fragments be made as large as possible. The products from the roll are put upon the bolting machine and the coarser portion, including the bran and many larger fragments of the interior of the grain, is bolted off and carried to a second pair of rolls, where the process is repeated. This is again repeated and so the bran finds its way through several pairs of rolls. Each time a considerable quantity of the fragments of the interior portion of the grain are broken off, and by successive bolting and purification the fragments are obtained comparatively free from bran. These fragments are divided into various grades according to their purity, size, etc., and crushed to fragments between various pairs of smooth rolls. The fragments are called middlings. They can be made very pure, and when crushed to flour make an article which is very free from the material which commonly finds its way into the feed. It is to flour produced in this way that the name patent flour is given. Not all of the flour contained in the grain can be obtained in the form of middlings of such character that they can be sufficiently purified to make a better grade of flour. The remaining portion is mixed with fine fragments of bran and often of the germ which is the embryo of the kernel. This portion of the flour is generally named clear grade flour. It is darker in color than the patent flour, and when separated in this way is inferior for bread-making purposes because of the impurities which it contains. When the clear flour and the patent are united in one, they constitute a straight grade flour, which, while superior to the flour made by the old stone mill process, has more nearly its same general character. The improved process of milling has enabled the miller to produce a greater quantity of flour from the wheat as well as flour of a superior quality, for by the old stone method it was impossible to remove all the flour from the bran without also grinding up with the flour an excessively large portion of the bran. From a food and economic standpoint, the clear flour is superior to the patent flour because it contains more of the protein, more of the fat and less of the starch. The same is true of the straight grade flour, for it contains

the excess of these ingredients found in the clear, and at the same time the objectionable qualities of the clear are largely removed, because the impurities thus more diluted are, except as to color, more beneficial than injurious. The color of the flour which is removed by the bleaching process is distributed throughout the entire flour-producing portion of the wheat grain, but is more abundant in the portion nearest to the bran, which is also the most nutritious. It is the purpose of the modern bleaching process to remove the yellow color instantly. It should be clearly borne in mind, in this connection, that the yellow color which is removed by the bleaching process is entirely independent of any dark or inferior color produced by the presence of the bran which is ground up with the lower grades of flour.

The writers were given the opportunity to examine the first samples of flour bleached by the Andrews process which were brought to this country. A careful comparison of the bleached and unbleached flour was made by us and published in milling journals.[4] Our examination of these flours was very thorough, and although we set about the analysis with somewhat prejudiced minds, we were unable to find any objections whatever to the sample of bleached flour, or any material differences between the two flours except that which was apparent in the color. Our findings with regard to this matter were put before the millers by one of the writers at the Operative Millers Convention, at St. Louis, and by the other at the meeting of the Federation of Millers at Buffalo. Shortly after this time and since, other investigators have made a careful study of the subject of bleaching flour and all, with the exception of two, have arrived at substantially the same conclusions that we gave in our first article and public lectures. Those prominent in these investigations are Fleurent,[5] of France, Prof. Harry Snyder,[6] of the Minnesota Agricultural Experiment Station, Prof. Ladd and Mr. Stallings,[7] of North Dakota, Dr. Avery[8] and later Prof. Alway,[9] both of the University of Nebraska, and lately Dr. Ludwig Weil,[10] Strassburg, Germany.

It has already been stated that the active agents in the bleaching of flour are nitrogen oxides and nitrosyl chlorid. Both of these substances result in decomposition products which give the usual test for nitrites. The test which is commonly used for detecting small quantities of this substance is known as the Griess-Ilosvay test, which is among the most delicate tests for any substance which is known to chemists. So delicate is this test that, according to Warrington, it is capable of detecting one part of nitrous anhydride in a billion parts of water. It was because of this very delicate test that it was possible to discover the residues of these gases in the flour.

The chemistry involved in the bleaching of flour has received much attention by us. We have isolated the coloring matter and have identified it or at least have established a very close relationship for it with other natural vegetable colors. It is not the province of this article to go into this phase of the question. The chemistry of this reaction will be taken up by us in a later article. The coloring matter of flour is the one material which shows the great avidity for uniting with the gases which are used in bleaching. The action on the coloring matter is instantaneous, and the amount required for the purpose of bleaching the flour is very minute. If an excess of the gas is used, it will eventually combine with other substances, primarily the gluten and finally the oil. It is only when the flour is overbleached and ruined that the action on these constituents of the flour is sufficient for it to be detected either by chemical or by physical properties.[11] It was conceded in the flour bleaching case conducted in North Dakota, as well as at the hearing in Washington, D. C., that the average amount of nitrite-reacting nitrogen in commercially bleached flours is practically one part per million. In our own experiments we have often found much less than this amount. It has been still further conceded[12] on the part of even those opposed to the bleaching of flour that only a small proportion, and in some instances not any, of the nitrite-reacting nitrogen is present in the bread. We have found this disappearance of nitrite-reacting nitrogen to be due in a large measure to the action of the yeast which is used in the bread.

The nitrite-reacting material of flours is also removed by the action of heat. This may be clearly shown by the tables given below. Quantities of spring patent flour were dried over night, and in the morning examination for nitrites was made in the usual way.

Temperature of oven.	Part per million nitrite-reacting nitrogen.
105° C.	None.
75° C.	0.22
40° C.	0.37
Not dried	0.37

Four lots of spring patent flour or 20 grams each were made into a sponge dough and put in the proving case over night. In the morning it was found the temperature had risen somewhat above 100° F. The flours were tested in the morning for nitrites in the usual way.

Yeast in dough.	Nitrite-reacting nitrogen
None	None
1 Gram	None
2 Grams	None
1 Gram plus chloroform	0.37
In original flour	0.37

Four lots of spring patent flour of 20 grams each were made into dough as on the preceding day and allowed to stand over night at room temperature. Determinations of nitrites were made in the morning.

Amount of yeast.	Parts per million nitrite-reacting nitrogen.
None	0.37
1 Gram	0.031
2 Grams	0.018
1 Gram plus chloroform	0.37
In original flour	0.37

It will be noted that in the first experiment where the flour is dried over night at a temperature of 105° C. that all of the nitrite-reacting nitrogen disappears. At a temperature of 75° C. it is reduced from 0.37 to 0.22. At a temperature of 40° C. no change takes place. In experiment No. 2 it will be noticed that from flour made into a dough with water and allowed to ferment in a proving case all of the nitrite-reacting nitrogen disappears. The same is true when 1 gram and 2 grams of yeast are added to the flour before making a sponge. When, however, chloroform was added to stop the action of yeast and bacteria, the nitrites remained as in the original flour. In the third experiment we notice that this change does not take place in the sponge made directly from flour without the addition of yeast when kept at ordinary room temperature. Better action takes place, however, when one and two grams of yeast are added to the flour. There is a reduction then from 0.37 to 0.018. In the third experiment the nitrite-reacting nitrogen would have all disappeared had the correct incubating temperature been used, except when chloroform was added. From the results of this experiment we see that drying at sufficiently high temperature dispels all of the nitrite-reacting nitrogen and that living bacteria and yeast consume it.

That the presence of even considerable amounts of nitrite-reaction nitrogen in flour acts favorably to the development of yeast in dough and not as a preservative is apparent from the following:

TABLE SHOWING THE INFLUENCE OF SMALL QUANTITIES OF ADDED SODIUM NITRITE ON THE EXPANSION OF SOFT DOUGHS.

	Added nitrite nitrogen in parts per million of flour.	Total volume of dough. H. S.	L. S.
Blank	0.0	800	860
1 cc. 1% nitrite of soda	20.3	900	860
5 cc. 1% " " "	101.5	860	900
10 cc. 1% " " "	203.0	840	900
20 cc. 1% " " "	406.0	300	260

In making the above expansions 100 grams of Pillsbury's best flour were used in each dough in connection with the following other ingredients: water, 75 grams; yeast, 10 grams; sugar, 3 grams. Total dough, 188. In those doughs in which the solution of nitrite was used it was made to take the place of the other water used so that all the doughs contained the same amount of liquid. Expansions marked L. S. were at slightly higher temperature than those marked H. S., the temperature of the two lots being about L. S. 95° F. and H. S. 90° F.

It will be seen from the above that no effect injurious to the expansion of the dough is apparent when a quantity of nitrite-reacting nitrogen is added to the flour in quantities 200 times as great as is present in commercially bleached flour. On the other hand, we find this larger amount to be beneficial to such expansion. It was also found that when bleaching gases are added to the flour sufficient to produce nitrite-reacting nitrogen to the extent of 60 parts per million, the flour was entirely destroyed for commercial purposes because of the well-known xanthoproteic reaction whereby the flour was highly discolored, producing a reddish yellow shade, and because the character of the gluten was changed by the action of this large amount of the acid-producing gases upon the gluten. Even in this aggravated condition the growth of the yeast was not prevented and the bread-making property of the flour was not destroyed, although the bread was of inferior quality. Attention should be called to the fact that in the experiment noted above sodium nitrite was used, while in the gas-treated flour the sodium was not added, the acid in this case being in part at least united with the gluten, forming with it the well-known class of syntonin bodies. It is known[13] that bodies of this character are continually formed during the process of bread-making by yeast, and are an essential step in such process of bread-making.

One of the contentions of those who are opposed to the bleaching of flour is that it leaves a deleterious substance in the nature of a preservative in the flour. The experiment cited above in which we have shown that the bacteria and yeast consume the nitrite-reacting material of the flour is sufficient answer to this contention

We have been making daily examinations of flour received from all parts of the United States and from foreign countries, including Canada, England and South America. This has naturally brought us in contact with flours of all kinds, from all classes of wheat, and representing all methods of milling. This work has been done for the purpose of ascertaining the bread-making and commercial value of these flours. During the last five years probably 90 per cent. of the flours which we have received have been bleached, and we have not in a single instance found any flour which appeared to be in any way injured by the process of bleaching. The analyses which we make of these flours are very thorough, as the commercial value, which depends on the quality of the bread, is based on our reports. In addition to this general analytical work on flours, we have made a thorough and exhaustive study of many flours, bleached and unbleached, to determine any effects which might have been produced by the action of bleaching gases upon the bread-making qualities of the flour. We have found that in every instance the only essential change in the character of the flour was in a whitening of the color and in some instances an increase of the water-absorbing capacity of the flour. Where there has been any slight difference in the volume of the bread, which could not be attributed to natural variation in the work, it has been, if anything, slightly in favor of the bleached flour. The same is true of the number of loaves of bread which are produced from a barrel of flour. The amount of yeast necessary for the production of bread from bleached flour, which we always call the fermenting period, was in no way increased over that required for the unbleached flour. The quality of the gluten, as shown by its capacity for expanding into a good-sized loaf of bread, has not been found to be in any manner injured. The average value, which in our report is based upon the color of the flour, the character of the bread, the amount of bread and the size of the loaf, was a little higher for the bleached flour than for the unbleached, because the color of the flour and the color and quality of the bread were improved. The flavor of bread is subject to much variation, due to the methods of bread-making, and is also one of the most difficult points to determine in the comparison of breads under examination. We have made careful comparisons along this line and have been unable to detect any deterioration of flavor when both flours, bleached and unbleached, were submitted to the same process of bread-making. We have already called attention to the fact that the patent flour, as compared with the clear, is relatively deficient in protein, fat and mineral matter, and for this reason possesses less nutritive value than the clear flour. We have also pointed out that when these two flours are combined they constitute the straight grade flour which is intermediate in character between the patent and the clear. While an experienced eye can readily distinguish between the grades of flour used when a straight grade flour from which the color has been removed is baked into bread and compared with bread from a patent flour from which the color has not been removed, it is our experience that preference will be given to bread made from the straight grade flour.

TYPICAL ANALYSIS OF BLEACHED AND UNBLEACHED FLOUR.

	Standard spring patent bleached.	Spring patent not bleached	Hard winter wheat bleached.	Hard winter wheat not bleached.	Durum bleached.	Durum not bleached.
Gluten, per cent...	11.0	11.0	11.5	11.5	10.5	10.5
Ash, per cent......	0.42	0.42	0.40	0.40	0.60	0.60
Absorption, per cent.	61.0	61.0	62.0	62.0	61.0	61.0
Color.............	100.0	99.0	100.5	99.0	97.5	95.0
Loaves, per bbl....	100.0	100.0	100.6	100.6	100.0	100.0
Size of loaf........	100.0	100.0	100.0	100.0	98.0	98.0
Quality of loaf.....	100.0	99.7	100.3	99.7	99.0	98.0
Average value.....	100.0	99.7	100.4	99.8	98.6	97.7
Fermenting period	100.0	100.0	102.2	102.2	97.7	97.7
Quality of gluten..	100.0	100.0	97.8	97.8	102.4	102.4

NUTRITIONAL EXPERIMENTS.

Twenty-four white rats were purchased of a rat dealer in Chicago during the month of July, 1908, the lot including 10 females and 14 males. These were put in several cages, weighed after dividing, and arranged on shelves in a cool, well-ventilated room, where all were given similar treatment as to food, water and ventilation. Boxes suitable for their protection and comfort were put in each cage. On the 28th of July the rats were arranged so that each of two cages should contain seven males, and each of two others should contain five females. An effort was made to have the weight of males in the two cages about equal and also the

weights of females of the two cages about equal. The experiment in feeding was begun on the 28th of July. Within two or three days one of the rats died from causes common to rats and in no way connected with the experiment. The weights of the rats at the beginning and end of the experiment are shown in the table given below:

WEIGHTS AND GAIN OF RATS.

	Flour bleached.			Flour not bleached.		
	5 Females.	6 Males	11 Total.	5 Females.	7 Males.	12 Total.
July 28	325.0 g.	482.0 g.	807.0 g.	329.0 g.	553.0 g.	882.0
Oct. 14	425.0 g.	572.0 g.	997.0 g.	439.0 g.	670.0 g.	1102.0 g.
Gain	100.0 g.	90.0 g.	190.0 g.	110.0 g.	117.0 g.	227.0 g.
Gain %	30.8%	18.6%	23.5%	33.4%	21.1%	25.7%

Figures show weight in grams and also gain in per cent. of the original weight.

A barrel of flour was procured from the Berger-Crittenden Milling Company, of Milwaukee, which was known at that time to have no bleacher, and which was fully borne out by tests to be entirely unbleached. Soon after receiving at the laboratories, the flour was put into four 50-pound tight tin flour bins for preservation. The flour from one of these bins was passed through the gases of the Alsop bleaching machine in a manner identical with that used in the flour mills. The time required for the passing of the flour through the gases produced from a generator suitable for a 100-barrel mill was two minutes. Tests were made for the amount of nitrite in the flour bleached in this manner, and the nitrite-reacting nitrogen was found to be three-tenths parts in a million. The flour was again run through the bleaching machine in the same manner as at first and the nitrites again determined. The amount found after this second bleaching was 0.56 part per million of nitrite-reacting nitrogen. On the following day biscuit was made from the bleached and unbleached flour. No nitrites whatever were found in either the flour or the biscuit unbleached. In the biscuit from the bleached flour the amount of nitrites found was equivalent to 0.3 part per million of nitrite-reacting nitrogen. It was considered that the bleaching of this flour had not been sufficient to meet the objections which might be raised as to its having been given sufficient treatment, and it was put through the bleacher twice more in the same manner as already described. After this last bleaching the nitrite determination was again made upon the flour on July 31, and was found to be, on the flour four times bleached by the Alsop machine, equivalent to 0.79 part of nitrite-reacting nitrogen per million. The flour was now put aside in the laboratory for use in the making of bread and biscuit for the experiment. The composition of these flours before and after bleaching was determined in the usual manner in which we determine the characteristics of different flours in making our commercial laboratory reports, and the results are given herewith:

	Spring patent.	6796	6796 bleached.
Gluten, per cent	10 5	11.0	10.9
Ash, per cent	0.42	0.49	0.49
Absorption, per cent	62.0	62.0	62.0
Color	100.0	99.0	99.5
Loaves, per barrel	100.0	100.0	100.0
Size of loaf	100.0	100 0	100.0
Quality of loaf	100.0	98.7	99.0
Average value	100.0	99.4	99.6
Fermenting period	100 0	102 5	102.0
Quality of gluten	100.0	97.5	98.0
Moisture	....	12.85	12.0
Acidity, as lactic acid	....	0.117%	0.117%

The bread used in these experiments was made substantially as follows: 500 grams of each flour were mixed with 310 cc. of water, 12 grams of compressed yeast, 15 grams of sugar, 7.5 grams of salt and 15 grams of lard. The dough was allowed to develop for two hours with one working, which working was done at the end of the first hour. At the end of the two hours the dough was molded into a loaf and put in the pan, where it was allowed to prove until it was ready for baking in the oven. It was baked usually in the electric oven until sufficiently done, requiring about 45 minutes. It was then taken out of the oven, cooled, and subsequently put in suitable tin boxes to preserve for the experiments. A portion of the time biscuits were substituted for the bread, so that the rats might have some variety of diet, and so that the teeth of the rats might be kept in somewhat better condition by their gnawing the harder biscuit. The biscuits were made substantially as follows:

Two hundred and fifty grams of each flour, 115 grams of water, 2 grams of salt, and 5 grams of Dr. Price's cream baking powder were mixed together, rolled to suitable thickness, cut with a tin biscuit cutter, put in a pan and baked in the electric oven. The amount of nitrites remaining in the bread and biscuit was determined on many of the samples, and the average amount found was 0.03 part per million of nitrite-reacting nitrogen for the bread and 0.24 part for the biscuit from the bleached flour. The average amount of nitrite-reacting nitrogen in the bread from the unbleached flour was none and in the biscuit from the un-

bleached flour was 0.02 part per million. The bread in these experiments was purposely made by an unusually short process, which would tend to leave in it much more nitrite-reacting nitrogen than would remain when the bread is given the usual amount of fermentation. Even in this short process of bread-making the nitrites were in many instances entirely removed. The rats were fed night and morning of each day and were supplied with sufficient water in a suitable tin vessel placed in their cage. The amount of bread or biscuit given at each feeding was equivalent to about 5 per cent. of the weight of the rats daily. This amounted to about 50 grams for the rats fed bleached flour and a trifle more for the rats fed unbleached flour.

The supply of bleached flour used in feeding these rats was exhausted about the 3rd of October, and another quantity of the same flour was run through the bleaching apparatus three times, in the same manner as on the previous occasion. The amount of nitrite-reacting nitrogen in the flour thus bleached was 1.56 parts per million, which was much in excess of what would possibly be introduced into the flour by a single bleaching. The rats were fed on bread and biscuit from this flour for about one week. The amount of nitrite-reacting nitrogen in the biscuit from this flour was 0.6 part per million and from the bread was 0.3 part per million.

At the end of the feeding period a considerable number of the rats were dissected by the Biological Division of the Columbus Laboratories under the direction of Dr. Adolph Gehrmann, and the data obtained in this manner is given below:

Notes on individual rats as dissected: The rats were killed with chloroform, stretched in a proper manner, and opened by a ventral incision extending the entire length of the body. Examinations were made on the following points, and where normal no mention is made of them in the following notes:

Nutrition and blood supply of intestines; general condition of intestines, stomach, liver, kidneys, spleen, heart, lungs, and also of amount of fat in mesentery and omentum. Portions of organs, as follows, were removed and put into a seven per cent. solution of formaldehyde for subsequent examination under microscope: Anterior portion of right lobe of liver; one-half of left kidney; middle portion of stomach including portions of the cardiac and pyloric ends; one-half of spleen and such other special portions as occasion required. The remaining portions of each rat were also preserved in formaldehyde for any future examinations which might be desired.

NOTES ON SERIES FED BLEACHED FLOUR.

Cages 1 and 2.

Rat No. 1. Stomach partially distended with food.

Rat No. 4. Tapeworm in intestines.

Rat No. 7. White nodule of fat within capsule of left kidney. 1/2 right kidney taken for microscopic examination.

Rat No. 11. Nothing abnormal found.

Rat No. 13. Much congestion of abdominal vessels. Stomach distended with gas; small ulcer on interior wall. Tapeworm in intestines; hydatid cyst in liver. Hardly any fat in mesentery. This was the most unthrifty rat in the experiment.

Rat No. 16. Intestines somewhat congested; hardly any fat in the mesenteries.

Rat No. 23. One of the most thrifty-looking rats in the entire experiment. No defects of any kind whatever found.

SERIES FED FLOUR NOT BLEACHED.

Cages 3 and 4.

Rat No. 2. Stomach fairly well distended with food. Examination showed nothing abnormal.

Rat No. 5. Tapeworms in small intestines. Spleen appeared somewhat small.

Rat No. 8. Normal appearance throughout.

Rat No. 10. Apparently abnormal contraction between cardiac and pyloric ends of stomach causing hour-glass shaped organ.

Rat No. 14. Some congestion of abdominal blood vessels. Small intestines contained three very large tapeworms. Stomach somewhat distended with gas. Darkened spots on anterior portion of anterior lobe of liver. Spleen presented irregular mottled appearance. Slight consolidation in upper lobe of left lung.

Rat No. 17. Small tapeworm in small intestine.

Rat No. 18. Some gas in intestines. Some tendency toward diarrhea. Small infiltration of fat into capsule of left kidney.

Rat No. 19. Slight congestion of small intestines. One very large tapeworm in small intestines.

IRREGULARITIES FOUND CLASSIFIED AS TO ORGANS EXAMINED.

Nutrition and Blood Supply of Intestines.—Some congestion of abdominal blood vessels found in

rat No. 14, unbleached series, and much in rat No. 13 of bleached series.

Abnormal Condition of Intestines. Tapeworms found in rats Nos. 4 and 13 of bleached flour series; in Nos. 5, 14, 17 and 19 of unbleached series. Some inflammation in rats Nos. 13 and 16 of bleached series; also in rats Nos. 14 and 19 of unbleached series. Tendency to fermentation and diarrhea were noticeable in rat No. 18 of unbleached series.

Stomach.—Stomachs were more or less distended with gas in rats No. 13, of bleached series, and No. 14, of unbleached series. Rat No. 10 of the unbleached series showed marked hour-glass contraction between cardiac and pyloric ends.

Liver.—Hydatic cysts were found in rat No. 13 of bleached series. Darkened spots were found on the anterior portion of the anterior lobe of No. 14 of the unbleached series.

Spleen.—That of No. 5 of unbleached series was unusually small and that of No. 14 of the same series presented an irregular mottled appearance.

Kidneys and Renals.—Whitish nodules of fat were found within the capsules of one of the kidneys of No. 18, of unbleached series, and No. 7, of bleached series.

Heart.—No abnormalities were apparent.

Lungs.—Slight areas of consolidation in upper lobe of left lung of No. 14 of unbleached flour series.

Fat in Mesenteries and Omentum.—Deficient in mesenteries of No. 13 of bleached flour series, and in No. 16 of same series. Also in No. 14 of unbleached series.

SERIES FED ON FLOUR NOT BLEACHED

No. of rat.	Sex	Weight in grams	General appearance.
2	Male	132	thrifty
5	Female	82	fairly thrifty
8	Male	92	fairly thrifty
10	Male	83	not thrifty
14	Male	71	not thrifty
17	Male	79	not thrifty
18	Female	84	fairly thrifty
19	Female	76	fairly thrifty

The remaining rats of this series were thrifty in appearance except one female which did not appear thrifty.

SERIES FED ON BLEACHED FLOUR.

No. of rat.	Sex.	Weight in grams.	General appearance.
1	Male	110	thrifty
4	Female	110	thrifty
7	Male	120	fair
11	Female	83	not thrifty
13	Male	47	not thrifty
16	Male	74	not thrifty
23	Female	129	very thrifty

The unkilled rats of this series were of thrifty appearance.

A series of feeding experiments was conducted with rats covering a period of several months. The bread which they received was made from flour which had been bleached with nitrosyl chlorid gas. The general findings were substantially the same as in the experiment detailed above. There were noticed no nutritional disturbances of any kind, and the *post-mortem* examination showed no lesions which in any way could be attributed to the bread made from this flour. In addition to the feeding experiments conducted with the rats, we have fed the guinea pigs, which we have always on hand for experimental purposes, bread from bleached flour covering a period of more than six years. During this time we have never once noticed any symptom or sign in the health of the animals which could in any way be traced to the bread made from bleached flour. *Post-mortem* examinations never revealed any lesion which could in any way be associated with the food which they had been receiving.

Ladd[14] has given results of experiments where alcoholic extracts of bleached and unbleached flours were evaporated under specified conditions and the residue administered to rabbits. The extracts from the bleached flour were reported by him to have produced death in a short time, the *post-mortem* findings being those of a corrosive poison. These experiments have been carefully repeated by Prof. Haines and Prof. Snyder,[12] who were not able to obtain results showing any indication of poison in the rabbits.

In working in conjunction with Prof. Haines at the Columbus Laboratories in November, 1908, several lots of flour were taken for extraction with 90 per cent. alcohol following the same general lines of investigation as laid down by Ladd. The flours used in these experiments were Sunnyside, marked 6796 unbleached, the same bleached by passing through Alsop gases four times, and the same bleached by very excessive treatment with nitrosyl chlorid. The flour bleached by the Alsop process contained 2.8 parts of nitrite-reacting nitrogen per million; that excessively bleached by the nitrosyl chlorid was entirely destroyed for commercial purposes and contained 30 parts nitrite-reacting nitrogen per million. Of the three samples of 6796 each flour in lots of 750 grams each was put in each of two bottles and 1750 cc. alcohol added to each bottle, making a total of 1500 grams of each flour and 3500 grams of alcohol for each. These were agitated thoroughly during the after-

noon of the day, were allowed to settle over night, and the clear supernatant fluid was poured from each on the following morning. This liquid was filtered to remove any starch which might be carried over. The total amount of liquid obtained for the flour treated with nitrosyl chlorid was 1280 cc.; that for the flour treated by the Alsop process 1210 cc.; that for the flour not bleached was substantially the same. Each of these liquids was introduced into a heavy glass globe of about 1500 cc. capacity. Those having the larger amounts were divided in two portions and a part of the liquid evaporated off before the remainder was added. The globes were connected with Liebig condensers at the lower end of which was an Erlenmeyer flask with a wide neck and side tube such as is used for vacuum filters. The whole was then connected with the small vacuum pan in the laboratories. Two of the glass globes were put in a large dishpan filled with water and so arranged that heat could be applied. Two others were put in another pan in a similar manner. The evaporation was then done by the assistance of the heated water and the vacuum pan. The time required for the evaporation was six hours. The maximum temperature of the liquid in the several flasks was 48° C. The average vacuum as shown by the manometer connected with the vacuum pan was from 23.5 to 25.5 inches. The removal of the alcohol in this manner was quite complete, but to still further remove small quantities which were in the flask, each flask was closed with a pledget of cotton and placed in the incubator heated by one 16-candle power electric light so that the temperature was about 37° C. and allowed to remain at this temperature over night. In the morning there was no odor of alcohol in any of the flasks. The residue in the several flasks was of an oily consistency with some sediment which was not entirely soluble in the clear oil. The oil was carefully poured from the flasks containing the Alsop process bleach and the nitrosyl chlorid bleach on the samples of Sunnyside flour, and allowed to drain into beakers until no more oil would flow from the flasks. These two flasks were carefully broken and the material remaining in them scraped from the glass. The weight of the total residue obtained from the flask treated with nitrosyl chlorid was 8.9 grams, and that from the flask of which the flour was treated with the Alsop process was 6.746 grams. 3.266 grams of that taken from the nitrosyl chlorid flour were weighed and mixed with water and 2 cc. of 95% alcohol so that the total volume of the mixture was about 10 cc. This amount of fat corresponded to nearly 250 grams of flour. It was taken up by means of a small glass syringe and fed to a rabbit weighing 2130 grams. No ill effects were apparent in the rabbit. It went to eating vigorously in the course of 15 minutes and showed no symptoms of distress of any kind. The oil from the Alsop process bleached flour was divided into two portions as nearly equal as possible. The first of these was treated in the manner described above and given to a rabbit, but unfortunately the soft catheter at the end of the syringe was introduced into the trachea which led to disturbance in the breathing of the rabbit, so that it was considered advisable to kill it shortly after and find the cause of the distress. This was done, and a *post-mortem* examination showed the lungs to contain much foreign matter and naturally highly congested. The other organs were found to be perfectly normal. The remaining portion of the Alsop process flour extract was fed to another rabbit in the same manner as that fed from the nitrosyl chlorid bleached flour, and no indications of distress whatever were occasioned by this flour. The weight of the rabbit which was fed was substantially that of the other, 2100 g. Both rabbits were kept under observation for a considerable time and no indication of distress or unusual symptoms were apparent. The acidity of the alcohol extract was identical for the three samples of Sunnyside flour, the unbleached, that bleached by the Alsop process, and that strongly overbleached by nitrosyl chlorid.

In the flour bleaching trial[15] in England, Wilcox and Luff, working independently, repeated experiments with rabbits as outlined by Ladd using unbleached, commercially bleached and strongly commercially bleached flour, making all told more than 50 experiments and report that in these experiments they were in no instance able to kill the rabbits because of any poisonous substance in the extracts, or to produce any toxic symptoms other than such as might come from the alcohol which was administered in connection with the extract. Judge Pollock, of North Dakota, and Judge Warrington, of England, both having listened to the testimony detailed by Ladd and the other experimenters, as mentioned above, sum up in their decision that bleached flour does not contain a deleterious substance.

If we calculate that the total amount of nitrous and nitric acid which might be present in one of the flours which was used by Ladd[14] for his test, based upon double the amount of nitrite-reacting nitrogen found (3 parts per million) and all calculated to nitric acid, it would be equivalent to only 5.4 milligrams (1/10 drop) of nitric acid. This amount of nitric acid is practically 1/100 the medicinal dose of nitric acid as given in the U. S. Dispensatory, and according to Ladd's testimony the liquid administered to the rabbits was much greater in amount than necessary to produce the dilution specified in that work for internal doses of nitric acid. Under the circumstances we could not expect any corrosive action from this amount of acid, even assuming that it could have been separated out of the flour as free acid without in any manner combining with the organic matter of the flour and alcohol.

It has been asserted by Prof. Ladd and others testifying against the bleaching of flour that proof of the action of the bleaching gases upon the oil of commercially bleached flours was apparent from the altered iodin absorption of the oil. Careful work upon this point had been done by the United States Department of Agriculture, and the results of the work submitted as testimony in the North Dakota flour bleaching trial[14] in which it was shown that in nine cases out of ten in which the "unbleached" sample did not show the presence of nitrites the difference between the iodine absorption of the fat of the bleached and unbleached flours was within the limit of experimental error, and this, notwithstanding the limit of experimental error on this test for iodine absorption, was considered to be not greater than the very close figure of one-half of one per cent. The readiness with which oil of wheat takes up oxygen of the air in its preparation for analysis is a potent factor in altering the iodine absorption of the oil.

The same table of analysis also gives detailed results of a considerable number of the determinations of the acidity of the bleached and unbleached flours in which the difference between the considerable number of samples examined was again within the limit of experimental error. We ourselves have never found such increased acidity in our own experiments with commercially bleached flours. Even assuming it to exist to a slight extent, it would not act injuriously on the bread-making quality of the flour, for as already stated, the changes brought about by the action of acids produced during fermentation are among the constant and necessary steps in the preparation of dough for baking.

As throwing some light on the influence of the bleaching gases upon the digestive action of pepsin on the proteids of flour, we will give the results of the following digestion experiments: In each case 10 grams of flour were used, one unbleached, the other bleached, showing 2.8 parts of nitrite-reacting nitrogen per million. Each was treated with 50 cc. of the official pepsin and hydrochloric acid mixture and kept at animal temperature for one hour with occasional agitation. Then both were made up to 250 cc. with cold water and 50 cc. were filtered from each. These were examined by the Kjeldahl method in duplicate and the unbleached gave 0.0369 g. nitrogen, the bleached 0.038 g. in one set, and in the other set 0.0361 g. for unbleached, and 0.0375 g. for the bleached. We thus see that the peptonizing action of this enzyme was in no way retarded because of the presence of the nitrites.

Diazo Test.—100 grams of unbleached flour were introduced into a flask of about one liter capacity, and carbon dioxide passed into it for 1 1/4 hours with frequent vigorous agitation. Dilute hydrochloric acid which had been recently boiled was added warm and the mixture agitated. The evolved gas was then swept by a stream of carbon dioxide into a Schiff azotometer containing the usual solution of caustic soda. A small amount of gas passed to the top which could not be absorbed by repeated agitation. The volume of this gas was 1.4 cc. It was tested with a lighted paper. It did not burn nor did it support combustion when tested as indicated by Prof. Ladd.[14] The above experiment, carried on in coöperation with Prof. Haines, was carried out as detailed by Ladd[14] and used by him as testimony in North Dakota to show the presence of diazo compounds of the nature of tyrotoxicon resulting in bleached flour from the action of the bleaching gases upon the constituents of the same. The amount of gas which he obtained from the bleached flour is substantially the same as we obtained in the above experiment from unbleached flour, and is undoubtedly air which adheres to the particles of flour and which cannot be removed even by the most careful and persistent treatment with carbon dioxide. That the experiments tend to show the presence of tyrotoxicon, or that such tyrotoxicon would be formed by the action of bleaching gases

on flour is not probable when we remember that this material, as found in cheese and other milk products, is wholly the result of bacterial growth, and that it is of an exceedingly unstable nature.

Nitrites and nitrite-reacting substances, which form the chief basis of the contentions of the opponents of bleached flour against that material, are very widely distributed throughout the mineral, vegetable and animal kingdoms. We have entered more into detail in the question of this distribution in a former paper,[16] and will summarize the facts only very briefly here. Nitrites are found in many drinking waters. They are objected to in that connection because their presence is an indication of the bacteriological or sanitary condition of the water, and not because of poisonous qualities of the nitrites themselves. Nitrites are found in considerable quantities in soils and in such common foodstuff as salt, baking soda, and baking powder. They have been found in small quantities in green vegetables including celery and other articles of food. They have been found in considerable quantities in preserved meats, especially those in the preparation of which saltpetre is used and the formation of nitrites is apparently an essential step in the preservation of meats by saltpetre. We have found in ham bought in the open market as high as five parts per million of nitrite-reacting nitrogen, or five times the average maximum amount found in commercially bleached flour. Nitrite-reacting nitrogen is found in all parts of the animal body, and is nearly always present in comparatively large quantities in the human saliva, including the normal saliva of healthy nursing infants. We have found in the saliva of man as high as 13 parts per million of nitrite-reacting nitrogen, which is 13 times that found in bleached flour. While nitrite-reacting nitrogen can nearly always be found in flours which have been bleached with oxides of nitrogen, the presence of nitrites in flour is not a proof that they have been bleached, as shown by Weil[10] who has obtained reaction for this substance by the Griess-Ilosvay test in samples of unbleached flour and in wheat which he has examined.

After having devoted much time during the past several years to a careful study of the question of flour bleaching in all its relations,[17] we would sum up our findings briefly as follows: The essential action of the bleaching of flour is to remove from it a small amount of yellow color which in itself is in no wise a valuable constituent in the flour from a food standpoint, and the presence of which is objectionable because it detracts from the flour in the eyes of the consumer by whom the demand for flour is created. The best results are obtained by its use only when thorough purification and cleaning are adopted, and it in no way contributes to the covering up of an unsound or damaged condition in the wheat. Any imperfections in purification or cleaning are made more apparent by the bleaching because these defects are in a manner covered by the coloring matter when it is present. Any improvement in quality brought about by removing an unusually large amount of color present in a flour which was inferior because of the presence of such excess of color certainly cannot be looked upon as in any way injuring or deceiving the consumer, as has been contended by some, for the cause which produced the inferiority now no longer exists. The purpose of the bleaching is to remove and not to conceal the inferiority. The prohibition of the bleaching of flour will curtail the use and cut down the price of durum wheat and all wheats which have an intense yellow color in spite of the fact that aside from this some of these wheats produce flour of the very highest quality. The effect of this is naturally felt more by the producer of wheat and the consumer of flour than by the miller whose prices are regulated by market values and competition. The most searching investigations have failed to show the presence in the commercially bleached flour of any substance that in the minute quantities in which it is present is in any way injurious to the bread-making qualities of the flour, or is in any way poisonous or has any toxicological or preservative action, or any action which is prejudicial to digestion or nutrition.

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THE COLUMBUS LABORATORIES.
CHICAGO.

THE TITANIUM ARC.

BY ISADOR LADOFF.

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I was fortunate to be present when Dr. E. Weintraub succeeded in striking an arc between two mercury terminals *in vacuo* by his ionization method at the Research Laboratory of the General Electric Co., then just called into existence by the sagacity of Mr. C. P. Steinmetz.

The mere fact that metallic vapors, even under such artificial conditions as a high vacuum, could give so much light was a revelation to me. I, of course, noticed the undesirable color of the arc and even at that time considered the mercury of very limited importance as a source of illumination. However, I realized fully the immense scientific interest of this arc. The idea occurred to me that some metals, or combinations of metals, might be found which would give satisfactory arc light illumination in the free air.

Since that time the idea of a metallic arc in the open air for lighting purposes turned into a fixed idea with me. In the spring of 1902 I was occupied in eliminating from a molten bath of copper the occluded gases. The color of the copper vapors, by a very natural association of ideas, recalled to my mind the mercury arc. I then started to study the voltaic arc, with the view of advancing my scheme of a metallic source of illumination in the open space.

It is a matter of common knowledge that carbon possesses the highest point of electro-vaporization among all-non-metallic elements known to chemistry and that carbon was therefore considered as the only material so far available or arc lighting. The connection between the point of vaporization and intensity of the arc light could be easily explained by the following familiar analogy:

Water subjected to heating in a vessel absorbs the heat supplied to it until it reaches the vaporization point. From the time this temperature is attained all the additional supply of the heat energy is consumed in the work of evaporization. It is obvious that the heating of a black body like carbon, whose vaporization point is very high, must result in the manifestation of some other form of energy expenditure than mere vaporization. This form of energy is light. The higher the vaporization point of the body heated—the more intensely luminous must be its arc. In fact, its light must increase with the temperature. This is known to be strictly true of so-called black bodies, of which carbon is the nearest approach to theory. This line of reasoning compelled me to look for some metallic compound or metal having an electro-vaporization point nearest to that of carbon.

I ound that among all metals titanium possesses the highest point of vaporization,[1] and that this point is the nearest to the point of vaporization of carbon.

Another consideration in favor of using titanium as a material for arc light illumination was, that among all metals it furnishes the richest spectrum as far as the number of lines is concerned. Indeed, titanium excels all non-rare metals in the nature and extent of the light-giving part of the spectrum. Thalen counted 201 lines in the red part of the spectrum out of 6,556; about 4,163 in the violet. Leveyng and Dewar counted between the same four new ones and Corner 25 in the ultraviolet, together 230 lines, two in the red, 17 in the orange, 32 in the yellow, 70 in the green, 35 in the blue, 45 in the indigo and 4 violet lines. 118 Fraunhoffer lines were recognized in the photosphere of the sun; 32 of these were artificially restored by Leveyng and Dewar to their actual state.

One drawback possessed by titanium as a source of illumination is its comparatively low electric conductivity.

With this conclusion in my mind, I made a great effort to find out whether my purely theoretical considerations were corroborated by facts. I ransacked my memory and tried to get

[1] See Mendelejéff's tables.

as many compounds of titanium as I could and tried them in the arc. I recall especially a piece of metal, or rather alloy of metals, containing iron and titanium in unknown proportions. The arc was very brilliant and white. Evidently there was more than a mere fancy behind my theoretical conclusions. Unfortunately, I was at this time again prevented from following up this line of investigation.

Titanium belongs to that class of rare metals that are not rare. As a matter of fact, titanium is probably as abounding in nature as copper. The reason why titanium enjoyed the reputation of being rare is most likely the fact that its technical application was rather limited. Titanium compounds are used in coloring porcelain and artificial teeth, leather, etc. There were attempts made by English metallurgists, among others Mr. Mushet, to use titaniferous iron ores for smelting. Moissan was the first to prepare some impure metallic titanium. Mr. Auguste J. Rossi was the first to use titanium alloys for the purpose of improving steel.

In the spring of the year 1903 I started to investigate the best methods of manufacturing solid magnetite arc light pencils. The main defect of these pencils consisted in their high resistance to electricity at ordinary temperatures.

The pencils belonged to the second class of conductors, *i. e.*, oxidic bodies conducting electricity only at comparatively high temperatures. The first step toward improving the solid magnetite pencils consisted in reducing their electric resistance. The encasing in metallic (iron) tubes was a classical method. The iron tube served the same purpose as the glower or heater in the Nernst lamp. However, the defects of this method were many and varied. The resistance of the body of the pencil remained unaffected and the arc had the tendency to run from the body of the pencil, according to the line of least resistance, on the iron tube, causing a sudden drop of luminosity.

In the light of my investigations of the ferro-titanium arc, it appeared to me clear that the only way to perfect the magnetite pencils is to radically change their physical and chemical properties by reducing them to the metallic state. My first step in that direction was the elimination of the hematite from the composition of the body, which proved, among other things, the mythological nature of the "binding properties" of the red oxide of iron. The experiment leading to that elimination was conducted as follows:

I made up three sets of pencils under identically the same conditions and of the identical material and composition with the difference that in one case I put in the customary 20 per cent. of hematite, in the second case I omitted this 20 per cent. of hematite, and in the third case I made the body of the pencil entirely of the red oxide of iron. All pencils contained equal quantities of titanic acid. The best photometric results were obtained from the pencil principally composed of magnetite. The ordinary mixture containing 20 per cent. red oxide of iron in addition to magnetite furnished intermediary results.

I then followed up these experiments with a series of similar tests, proving conclusively that the deoxidation or metallization of the electrode must lead to technical and commercial success. The tests made proved that a reduced pencil gave twice the luminous efficiency of a non-reduced one, both containing equal quantities of titanic acid. Besides this the reduced pencils had the advantage that they could contain comparatively high quantities of titanium without turning inoperative. The metallic pencils possessed greater strength, uniformity, and a better appearance. Their resistance was reduced to negligible values. The process of oxidation going on in the arc liberated an immense quantity of heat, and in this way relieved the electric field of the necessity of generating it through the process of overcoming useless resistance.

The magnetite pencil was oxidic from start to finish. The metallic pencils presented three phases: The first phase was presented by the electrolytic or oxidic material used for the manufacture of the pencils—the oxygen compounds of iron and titanium; the second phase was covered by the metallic ready-made pencil; the third phase and final one consisted of the electrolytic or oxidic material resulting from the process of arcing.

The process of deoxidation or metallization is practically a process of storing up energy in the body of the electrode, the energy of combustion. The positive coefficient of the metallic pencil, *i. e.*, its property of increasing in electric resistance with rise in temperature was helpful in steadying the arc. In short, the magnetite pencil was by the process of metallization turned a technical and commercial success equal to that of the ferro-titanium electrode prepared from the alloy manufactured in the electric furnace.[1]

[1] The color of the respective arcs was, however, different The ferro-titanium made in the furnace was bluish white, white in the arc of the reduced pencil was rather yellowish white.

In order to determine the difference in the behavior of the pencils according to their conductivity, a number of them were partially reduced in carbon at 1,150° C. Their resistance varied from 11 to 28.56 ohms. Pencils heated without carbon at the same temperature at the same time showed a resistance varying from 5,400,000 to 9,830,000 ohms. As the degree of reduction seemed to me to play some rôle in the arc, I made a few experiments to determine the influence of the process of oxidation in the arc. Electrodes for these experiments were prepared in the usual way and manner. One batch contained the usual proportion of hematite and magnetite, the second batch did not contain any hematite at all, and the third batch did not contain any magnetite at all. All of these three batches contained an identical quantity of titanium oxide (of 7.5 parts) and all were treated at the same time under exactly the same conditions, as far as practicable. The most luminous arc was produced by the pencils containing only magnetite and titanium oxide; the least luminous arc was produced by pencils composed only of hematite and titanium oxide. The mixture composed of 80 parts of magnetite and 20 parts of hematite produced an arc of medium luminosity. As hematite represents the final product of oxidation of iron, the conclusion was near at hand that oxidation is a factor favorable for the luminosity of the arc, *i. e.*, the more space there is left for the oxidation of the material of the electrodes in the arc, the higher must be the luminosity of the arc.

For the purpose of verifying this conclusion, additional experiments were conducted. Electrodes of the identical batch were subjected to various degrees of reduction and the luminosity of their arc tested. In each case the more reduced pencils gave a higher luminosity, and the luminosity of the perfectly reduced pencils was about double that of the luminosity of the non-reduced pencils of the same batch. A batch containing 50 per cent. magnetite and 50 per cent. titanium oxides was subjected to various degrees of reduction with the following results:

Well reduced pencils produced an arc of a luminosity equal to	1271	candle	power
Partly reduced pencils produced an arc of a luminosity equal to	1000	"	"
Poorly reduced pencils produced an arc of a luminosity equal to	868	"	"
Non-reduced pencils produced an arc of a luminosity equal to	700	"	"

All these are horizontal measurements. The current used was a direct one of 3.4 amperes, with 75–80 volts drop across the arc. The volts of the standard were 30.1 of 63 candle power. The reduction not only about doubled the efficiency of the arc, but allowed the use of high percentages of titanium oxide in the mass of the pencils. In the non-reduced or partially reduced pencils an addition of about ten parts of titanium oxide was excluded, because it caused the arc to flicker to such an extent that no photometric reading could be taken with any degree of accuracy, if at all. The arc of the reduced pencils did not flicker very badly even when as high as 90 per cent. of titanium oxide was used in addition to 10 per cent. of magnetite as the mass for the pencils.

There appears, however, to be a limit beyond which any further addition of titanium oxide is not advantageous. The maximum efficiency of the arc is obviously not the only thing to be considered in our case. The best results obtained was with pencils containing about 50 per cent. of titanium oxide and 50 per cent. magnetite. The perfectly reduced electrodes were metallic through and through, harder than tool steel, and took an excellent polish. When ready for use they looked like ordinary steel cylinders.

From Auguste J. Rossi I procured technically important quantities of iron and titanium and also copper and titanium alloys. A series of tests convinced me of the high technical value of titanium alloys for arc light illumination. A patent, No. 840,634, was granted to me Jan. 8, 1907. The claims allowed are as follows:

1. An arc light pencil consisting for the most part of an alloy of titanium with another metal, possessing greater conductivity than titanium.

2. An arc light pencil consisting for the most part of an alloy of titanium with iron.

3. An arc light pencil comprising an alloy of titanium with other metals possessing greater electrical conductivity than titanium, said alloy constituting more than ten per centum of said pencil.

4. An arc light pencil comprising an alloy of titanium with iron, said alloy constituting more than ten per centum of said pencil.

5. An arc light pencil comprising an alloy of titanium with iron, said titanium constituting more than five per centum of said pencil.

6. An arc light pencil comprising an alloy of titanium with other metal possessing greater electrical conductivity than titanium, said titanium constituting more than five per centum of said alloy.

7. An electrode for arc lighting consisting of an alloy of titanium and other metals possessing greater electrical conductivity than titanium.

8. An electrode for arc lighting consisting of an alloy of titanium.

9. An electrode composed of ferro-titanium.

10. An electrode containing ferro-titanium.

11. An electrode containing considerable amounts of iron and titanium in metallic state.

12. An electrode formed from any alloy of iron and titanium containing about thirty-five parts of titanium and sixty-five parts of iron.

13. An electrode formed from an alloy of iron and titanium containing less than thirty-five parts of titanium and more than sixty-five parts of iron.

In order to ascertain the technical value of my invention I investigated a few samples of my arc light pencils. The samples were designated as follows:

B—2 pieces marked F. T.—80 per cent. ferro-titanium.

C—1 piece marked 41–L—30 per cent. rutile, 70 per cent. magnetite.

3–$^1/_2$ piece National plain carbon.

The tests were conducted at the laboratory of the Lamp Testing Bureau, now "Electrical Testing Laboratory." Tests were first made in a hand-fed arc lamp on a direct current circuit from a storage battery of 60 cells, giving 120 volts, approximately. Owing to the peculiar nature of the arc it was found impossible to maintain an arc in this style of lamp much above 3/8 inch in length, and from 48 to 55 volts.

The results of the candle power measurements and life tests of the ferro-titanium (B) and rutile (C) pencils, as well as tests made on a plain open arc domestic carbon, are summarized in Tables I, II and III. These tests are principally valuable as illustrating the nature of the pencils and relative illumination and life, as compared to an ordinary carbon when operated under the same conditions. The results as tabulated are the averages obtained.

The average results given were mostly obtained with a positive carbon pencil above. The results with a positive copper pencil above were slightly lower in candle power, but not materially so, and were averaged with the other results obtained.

The positive copper pencil is evidently only slowly consumed in the arc when used in connection with the titanium pencils. There is a slight loss in weight probably due to oxidation and scaling, at the surface of the copper owing to its high temperature.

The rutile pencil was further tested in a constant potential arc lamp operating on a current of 4.5 amperes approximately. In this lamp the rutile pencil (C) was placed below, ordinary carbon above, and the test made first with the carbon as a negative and then with it as a positive. As the rutile pencil could not be placed in the upper holder in the lamp for purposes of comparison, a further test was made in the hand-fed lamp, using rutile pencils both above and below, with the upper pencil positive. Two sets of measurements were made, one at 60 volts, approximately, and the other at 70 volts. The results are tabulated in Tables I, II and III:

TABLE I.—RESULTS OF TESTS IN HAND FED LAMP AT 3.5 AMPERES

	"B" Ferro titanium	"C" Rutile	"F." Plain carbons
Mean spherical candle power	510.0	283.0	84.0
Watts per candle power	0.579	0.701	2.5
Amperes	3.51	3.51	3.5
Volts	48.3	55.8	49.1
Watts	169.4	195.4	171.4
Length of arc (inches estimated)	0.375	0.350	0.125
Life of negative (hours per inches)	3.85	11.1	2.8
Diameter of pencils (inches)	0.57	0.52	0.50
Resistance per inch, ohms	0.00164	0.00284	0.0846

TABLE II.—LAMP AT 6.6 AMPERES

	"B" Ferro-titanium.	"C" Rutile.	"F" Plain carbons.
Weight per inch, grams	9.64	14.33	4.83
Mean spherical candle power......	968.0	737.0	243.0
Watts per candle power	0.341	0.436	1.35
Amperes	6.6	6.6	6.6
Volts	49.5	48.7	50.1
Watts	326.7	321.4	330.3
Length of arc, inches (estimated)	0.400	0.375	0.180
Life of negative (hours per inch)	1.1	1.96	1.7

TABLE III.—LAMP AT 9.6 AMPERES.

	"B" Ferro-titanium.	"C" Rutile.	"F" Plain carbons.
Mean spherical candle power	1135.0	Fused excessively with 9.6 amp.	485.0
Watts per candle power...........	0.330		0.986
Amperes	9.6		9.6
Volts	39.0		5 0
Watts	374.4		480.0
Length of arc, inches (estimated)	0.375		0.190

TABLE IV.—RESULTS OF TESTS WITH RUTILE PENCILS

At 60 Volts	Carbon upper —, rutile lower +	Carbon upper +, rutile lower —	Rutile upper +, rutile lower —.
Mean sperical candle power..	544.0	448.0	624.0
Watts per candle power	0.521	0.61	0.41
Amperes	4.52	4.18	4.25
Volts	62.8	64.8	61.2
Watts..............................	283.9	270.9	260.1
Length of arc (inches estimated)	0.75	0.75	0.70

The light distribution in the tests of the ferro-titanium, rutile and carbon pencils at 3.5 amperes and from 50 to 55 volts are shown in Fig. 1

(left side). The light distribution of the test of the rutile pencil in a constant potential lamp at 4.2 amperes and 70 volts is shown in Fig. 1 (right side).

TABLE V AT 70 VOLTS.

	Carbon upper , rutile lower +.	Carbon upper +, rutile lower —.	Rutile upper +, rutile lower .
Mean spherical candle power	469 0	590 0	1015.0
Watts per candle power	0 663	0 56	0 30
Amperes	4.35	4.35	4.30
Volts	71.5	72.0	70.0
Watts	311 0	314 0	301 0
Length of arc, inches (estimated)	0.875	0.875	0.75

All candle power measurements were made on the arc photometer designed by Prof. Matthews. The life of the results is computed from a burning test of from one and one-half hours to two hours, the pencils being first burned to shape and then weighed on a chemical balance before and after the test.

For the purpose of comparison, was plotted on Fig. 2 a curve "F" taken from the report of Prof. C. P. Matthews, included in the report of the Committee on the Photometric Measurements of Arc Lights to the National Electric Light Association, May 20, 1902. This curve is the result of many measurements and represents series enclosed lamps in common use in this country for street and interior illumination. The measurements were made on a constant current of 6.8 amperes with 70 volts at the arc, with an opalescent inner and a clear outer globe. In interior illumina-

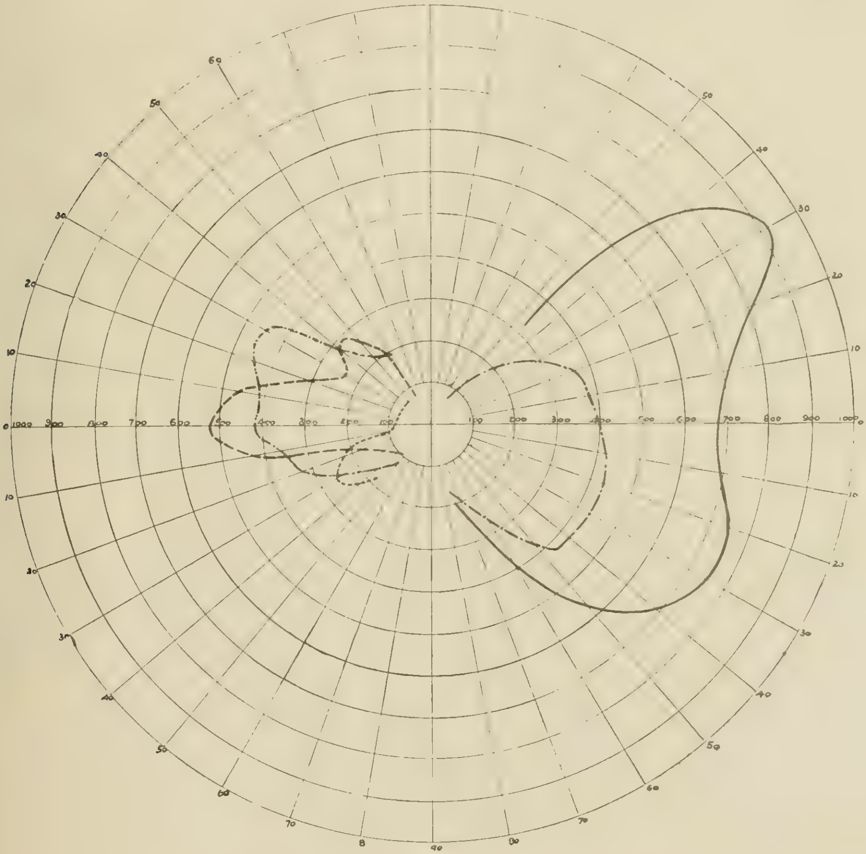


Fig. 1.

tion an opal or opalescent outer is usually substituted for a clear outer. The constant potential enclosed arc lamp is also used for inside illumination, but its light distribution curve for the same energy consumption does not materially differ from that shown.

The series enclosed arc lamp gives 303 mean spherical candle power at 476 watts or 1.57 watts per mean spherical candle power. They burn approximately 100 hours for one trimming.

The light produced by ferro-titanium and rutile (oxide of titanium and magnetite) pencils is a yellowish white as judged by the eye. The spectroscope shows the entire spectrum with special briliancy in the bright yellow portion and the neighboring light green and orange. The size and length of the arc, which produces most of the light, softens the sharpness characteristic of the open carbon arc. The arc itself presents many peculiar characteristics. The normal arc with a positive copper or carbon pencil above and the ferro-titanium or rutile pencil below is approximately 1/2 inch in length at from 50 to 55 volts, and increases to 3/4 or 7/8 inch at 70 volts. It is from 3/32 to 1/8 inch in diameter and seems to emanate from the titanium pencil. At the higher voltage the arc is very unstable and is easily broken in a hand-fed lamp without globe. At from 50 to 55 volts the familiar sound of a "hissing" carbon is produced. As the voltage and the length of the arc is increased this sound is diminished and the only sound produced is the one of escaping steam, but this is not of an objectionable character.

Under both the above conditions of operation the point of contact of the arc with the upper and lower pencils is constantly shifting, which causes a flutter in the light emitted. The objectionable features of this are largely eliminated with a long arc, and when protected by a globe.

The life tests were made from 50 to 55 volts, a much lower voltage than that at which the pencils are designed to operate. Therefore, while these tests are indicative of the results to be expected at 75–80 volts, the life at 75–60 volts cannot be predicted upon them. From these results, however, and from actual tests made with the necessary special apparatus by the writer and certified to by others engaged in the tests, it seems safe to estimate the life of a rutile pencil 1/2 inch in diameter to be from 10 to 12 hours per inch—perhaps higher, later tests showed 25 hours to one inch.

There should be no difficulty, therefore, in proportionating the size and length of the pencil to attain a life of 200 hours, the normal life of the en-

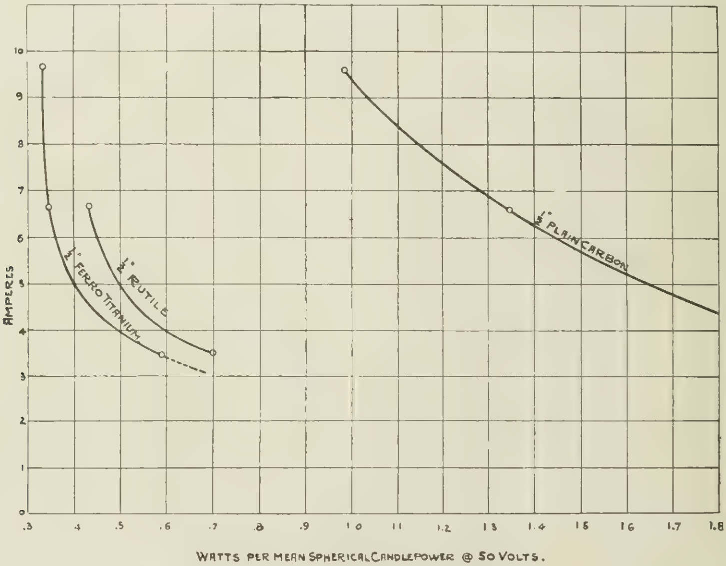


Fig 2

closed carbon lamp with one trimming. As the arc under proper conditions can be maintained at from 3/4 to 1 inch in length by increasing the diameter of the titanium pencil, the burning hours for one trimming could be very materially increased. This has actually been done and a very much higher life obtained.[1]

As already mentioned, when the titanium pencil is made the negative and placed below, at 70 volts, the arc is from 3/4 to 7/8 inch long and about 1/8 inch in diameter, and of an unusually white color, slightly more light being produced at or near the surface of the electrodes, owing to the concentration of the arc and the incandescence of the surfaces. The arc itself is clean cut and well defined, and is a true arc and not a flaming arc, as is generally understood by that term.

The same results were obtained with either a copper or carbon positive. As already mentioned, the arc fluttered and shifted constantly. The apparent trend of the arc and the gases and material carried by it was, under normal operation, from the negative to the upper positive pencils. Under the same current reversed, that is, the lower titanium pencil made the positive, an arc of entirely different character was obtained. The diameter of the arc was increased from 1/8 to 1/4 inch or 5/16 inch. At the same voltage the length was also slightly increased, approximately to an inch. The "flutter" as mentioned was absent, although the arc lazily shifted from one point to another. The direction of the arc still seemed to be from the lower positive to the carbon or copper negative above, but possessed very little illuminating power, and had a decidedly reddish tinge. Frequently, for short intervals, the arc became suffused with the white light characteristic of titanium. On account of its steadiness, lack of "fluttering" and very large diameter and length, the arc presents many attractive features.

By placing the titanium pencils on both sides of the arc and making the upper electrode positive, a third arc of a distinctly different character was obtained; though differing from either, it seemed to be practically a combination of the two above mentioned. The arc resembled an inverted cone in shape with an apex on the lower rutile negative pencil, and the base on the upper pencil. Through the center ran a core fairly representing the arc obtained in the first case above mentioned. Around it was a zone representing the second arc described but increased in diameter to possibly 5/16 or 3/8 inch and suffused with the white titanium incandescent gases. The arc thus obtained was absolutely steady with no fluttering or shifting. Both upper and lower pencils were fused at their surfaces, but contrary to expectations, the molten material upon the upper pencil did not drop. The light is softened somewhat by the presence of what might be called the negative arc, but possesses all the color characteristics of the titanium arc. The measurements made of these three arcs have been given in Tables IV and V, from which it is seen that the candle power efficiency is nearly doubled at 70 volts by placing the titanium pencil above as well as below.

An efficiency of 0.3 watt per mean spherical candle power was obtained in this test, and it seems entirely probable that this can be improved.

In Fig. 2 I have plotted the watts for mean spherical candle power obtained at 50 volts approximately, with 1/2 inch pencils, and at various current values. It is apparent from the curves there shown that there is very little increase in efficiency resulting from an increase of current above 6 amperes, under the conditions observed in the test, *viz.*, with 1/2 inch pencils and about 50 volts at the arc.

In Fig. 3 there were plotted the results obtained at 60 and 70 volts with a rutile lower negative, and a positive electrode of carbon and rutile, respectively. Unfortunately, the number of observations was not sufficient to construct a reliable

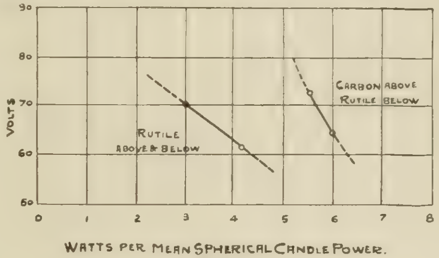


Fig. 3

curve, but the cut indicates graphically the great increase in efficiency due to using a titanium positive as well as negative, and from the direction of the curves it indicates that an increased efficiency would be obtained at a higher voltage, especially in the case where the titanium is used for both positive and negative electrodes.

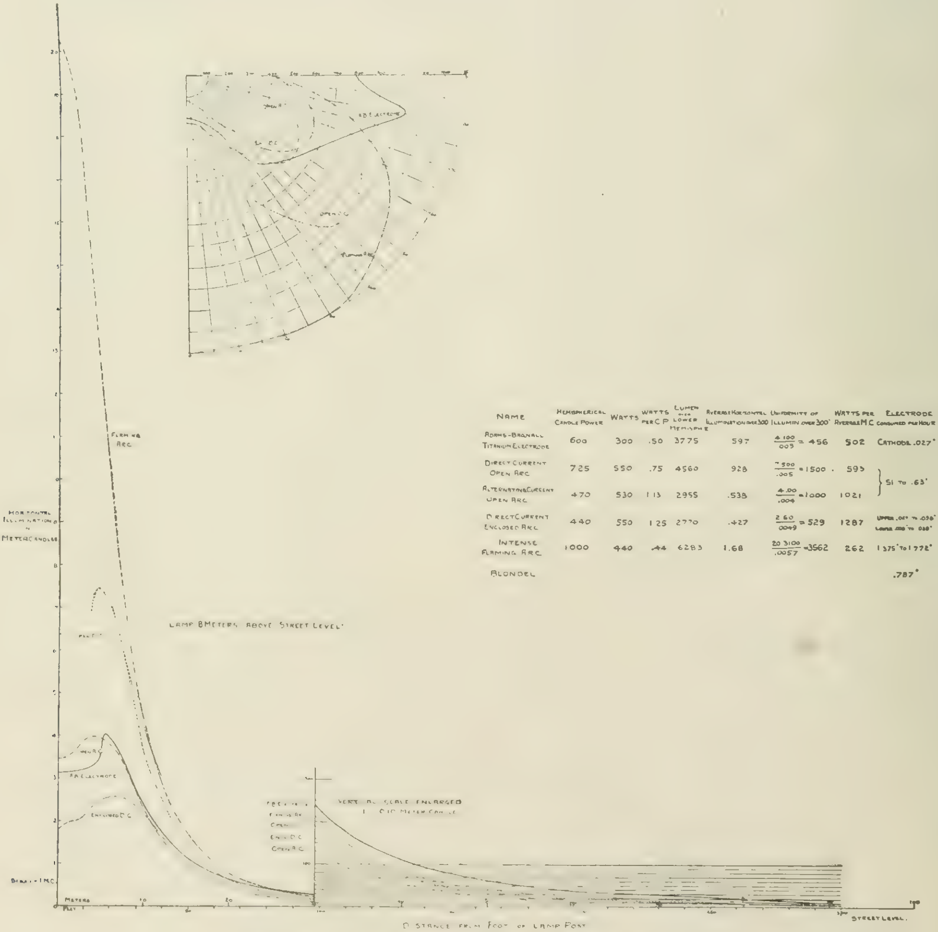
A very interesting phase of the investigation

[1] 30–35 hours per one inch.

of the titanium pencils was opened up by the chemical analysis to which the raw material and the ready-made pencils were subjected. The general opinion is, that titanium oxides can be reduced to the metallic state only at the high temperature of the electric furnace. However, the behavior of the reduced magnetite-rutile pencils was such as to suggest that at least a part of the titanic oxide was actually reduced to the metallic state.

The author thought that the oxygen compounds of iron may facilitate the reduction of the titanic oxide homogeneously intermixed with them to metallic titanium at a temperature of about 1200° C., in the presence of a reducing agent, like carbon, hydrogen, etc. For the purpose of ascertaining whether or not this hypothesis was correct, the analyses of the following bodies were carefully executed:

A. Ilmenite ore. B. Arc light pencil prepared as described above. C. Magnetite rutile pencil made of rutile and magnetic oxide of iron prepared as above described. D. Another sample of ilmenite in the shape of pellets. E. Pencils pre-



Name	Hemispherical Candle Power	Watts	Watts per C P	Lumen over Lower Hemisphere	Average Horizontal Illumination over 300	Uniformity of Illumin over 300'	Watts per Average M C	Electrode consumed per Hour	Watts per Hsphcl Lumen
Adams-Bagnall Titanium Electrode	600	300	.50	3775	597	$\frac{4.100}{.009} = 456$	502	Cathode .027"	.079
Direct Current Open Arc	725	550	.75	4560	928	$\frac{7.500}{.005} = 1500$	593	.51 to .63"	.121
Alternating Current Open Arc	470	530	1.13	2955	.538	$\frac{4.00}{.004} = 1000$	1021		.179
Direct Current Enclosed Arc	440	550	1.25	2770	.427	$\frac{2.60}{.0049} = 529$	1287	Upper .0[illegible] to .030"; Lower .0[illegible] to .038"	.198
Intense Flaming Arc	1000	440	.44	6283	1.68	$\frac{20.3100}{.0057} = 3562$	262	1.375" to 1.772"	.070
Blondel								.787"	

Fig. 4.—Comparative photometric values of the improved titanium electrode.

pared from the above pellets. F. Reduced ilmenite pellets. G. Pencils made from these very reduced pellets. H. Finally slag taken from the upper surface of the arc light pencils, after they were arced for a considerable time.

The analyses of these materials were as follows:

ANALYSIS A.—ILMENITE.

		Per cent.
Silica	(SiO_2)	3.40
Titanic oxide	(TiO_2)	41.70
Ferrous oxide	(FeO)	44.24
Alumina	(Al_2O_3)	3.64
Oxide of manganese	(MnO)	0.74
Oxide of chromium	(Cr_2O_3)	0.16
Lime	(CaO)	1.20
Magnesia	(MgO)	3.96
Oxide of copper	(CuO)	0.40
Phosphorus anhydride	(P_2O_5)	0.22
Sulphuric anhydride	(SO_3)	0.20
Alkalies	($Na_2O.K_2O$)	1.07
		100.93

ANALYSIS B.—ORE PENCIL FROM ILMENITE.

		Per cent.
Silica	(SiO_2)	3.87
Alumina	(Al_2O_3)	2.35
Manganese	(Mn)	0.50
Oxide of chromium	(Cr_2O_3)	0.24
Lime	(CaO)	1.32
Magnesia	(MgO)	3.93
Copper	(Cu)	0.32
Phosphorus	(P)	0.10
Sulphur	(S)	0.05
Alkalies	(Na_2O K_2O)	1.12
Carbon	(C)	0.50
Metallic iron	(Fe)	46.28
Metallic titanium	(Ti)	3.54
Oxides of titanium	(TiO_2 Ti_2O_3)	35.88 by diff.
		100.00
Total titanium calculated to higher oxide, TiO_2		46.52

ANALYSIS C.—RUTILE PENCIL MADE FROM MIXTURE OF THE MINERAL RUTILE WITH MAGNETIC OXIDE OF IRON.

		Per cent.
Silica	(SiO_2)	3.25
Alumina	(Al_2O_3)	1.77
Manganese	(Mn)	0.40
Oxide of chromium	(Cr_2O_3)	0.12
Lime	(CaO)	1.25
Magnesia	(MgO)	1.04
Copper	(Cu)	0.08
Phosphorus	(P)	0.10
Sulphur	(S)	0.05
Alkalies	($Na_2O.K_2O$)	1.80
Carbon	(C)	0.35
Metallic iron	(Fe)	48.93
Metallic titanium	(Ti)	3.24
Oxide of titanium	(TiO_2 Ti_2O_3)	37.62 by diff.
		100.00
Total titanium calculated to TiO_2		48.45%

ANALYSIS D.—SLAG MATERIAL FROM THE TOPS OF PENCILS THAT HAVE BEEN ACTED UPON BY THE ELECTRIC ARC.

		Per cent
Silica	(SiO_2)	2.60
Alumina	(Al_2O_3)	2.45
Manganous oxide	(MnO)	0.50
Oxide of chromium	(Cr_2O_3)	0.20
Lime	(CaO)	1.60
Magnesia	(MgO)	4.17
Copper oxide	(CuO)	0.30
Phosphoric anhydride	(P_2O_5)	0.03
Ferrous oxide	(FeO)	50.08
Titanium oxides plus alkalies by difference		38.07 by diff.
		100.00
Total titanium calculated to higher oxide, TiO_2		40.90%

ANALYSIS E.—ILMENITE PELLETS.

		Per cent.
Silica	(SiO_2)	3.50
Alumina	(Al_2O_3)	2.55
Ferrous oxide	(FeO)	44.68
Titanic oxide	(TiO_2)	37.90
Lime	(CaO)	1.02
Magnesia	(MgO)	3.46
Alkalies	(Na_2O K_2O)	0.60
Chromic oxide	(Cr_2O_3)	0.35
Oxide of copper	(CuO)	0.05
Suphuric anhydride	(SO_3)	0.41
Manganous oxide	(MnO)	0.25
Phosphoric anhydride	(P_2O_5)	0.035
Loss in ignition		4.93
		100.00

ANALYSIS F.—ILMENITE PENCIL FROM PELLETS.

		Per cent.
Silica	(SiO_2)	4.05
Alumina	(Al_2O_3)	2.40
Manganese	(Mn)	0.40
Oxide of chromium	(Cr_2O_3)	0.35
Lime	(CaO)	0.91
Magnesia	(MgO)	3.09
Copper	(Cu)	0.12
Phosphorus	(P)	0.03
Sulphur	(S)	0.06
Alkalies	(Na_2O K_2O)	1.30
Carbon	(C)	1.33
Metallic iron	(Fe)	45.00
Metallic titanium	(Ti)	5.22
Oxides of titanium	(TiO_2 Ti_2O_3)	35.10
		99.36
Total titanium calculated to TiO_2		43.80%

ANALYSIS G.—REDUCED ILMENITE PELLETS.

		Per cent
Silica	(SiO_2)	4.88
Alumina	(Al_2O_3)	3.40
Manganese	(Mn)	0.59
Oxide of chromium	(Cr_2O_3)	0.35
Lime	(CaO)	0.82
Magnesia	(MgO)	4.18
Copper	(Cu)	0.28
Phosphours	(P)	0.10
Sulphur	(S)	0.30
Alkalies	(Na_2 K_2O)	1.19
Metallic iron	(Fe)	45.40
Carbon	(C)	0.43
Metallic titanium	(Ti)	3.00
Oxides of titanium	(TiO_2 Ti_2O_3)	35.08 by diff.
		100.00
Total titanium calculated to higher oxide	(TiO_2)	40.40%

ANALYSIS II ILMENITE PENCILS FROM REDUCED PELLETS

		Per cent
Silica	(SiO_2)	3.95
Alumina	(Al_2O_3)	1.80
Manganese	(Mn)	0.14
Oxide of chromium	(Cr_2O_3)	0.22
Lime	(CaO)	0.65
Magnesia	(MgO)	3.11
Copper	(Cu)	0.16
Phosphorus	(P)	0.02
Sulphur	(S)	0.10
Alkalies	($Na_2O.K_2O$)	1.28
Carbon	(C)	0.82
Metallic iron	(Fe)	50.60
Metallic titanium	(Ti)	5.64
Oxides of titanium	($TiO_2.Ti_2O_3$)	31.51 by diff.
		100.00
Total titanium calculated to higher oxide	(TiO_2)	43.05

The mineral ilmenite is a ferrous titanate present in the sample under examination to the amount of 85.94 per cent., the remaining 14.05 per cent. represents the total percentage of the other minerals present in the chemical combinations shown in the report.

The ilmenite pencil consists of 46.28 per cent. of metallic iron, 3.54 per cent. metallic titanium and 35.88 per cent. of the lower and higher oxides of titanium, respectively Ti_2O_3 and TiO_2. The sum of the percentages of metallic iron, metallic titanium, and the oxides of titanium comprises 85.70 per cent. of the compounds reported in the analysis. The method of arriving at these figures is as follows:

The metallic iron was determined by treating the powdered pencil with a 20 per cent. solution of sulphuric acid with exclusion of air, namely, in a flask through which a current of carbonic acid gas was continually flowing. The ferrous sulphate solution thus obtained was titrated for iron with a solution of permanganate of potash by the well-known method. The presence of metallic iron was corroborated by the occurrence of small particles of metal which were found while powdering the pencil, these particles flattening out under the pestle and resisting reduction to the powdered state. These particles were also magnetic.

Another proof of the presence of a metal was the evolution of gas when the powdered pencil was treated with hydrochloric acid. Further evidence of the presence of metallic iron in the ilmenite pencil was the precipitation of metallic copper on treating the powdered pencil with a solution of copper sulphate.

The metallic titanium was found by treating the powdered pencil with strong hydrochloric acid, filtering the liquid and determining the titanium in the clear solution. That this was metallic titanium that was dissolved, and not the oxide, is borne out by the investigations of Henry Moissan, who, in his "Treatise on the Chemistry of Minerals," Paris, 1905, states that ignited oxides of titanium Ti_2O_3 and TiO_2 are not soluble in hydrochloric or nitric acids. The same facts are reported in published results of the investigations of Ebelman (see Roscoe and Schorlemmer's "Chemistry," Volume II), where it is stated that the ignited oxides of titanium Ti_2O_3 and TiO_2 are not soluble in hydrochloric acid. Again, in Watts' "Dictionary of Chemistry," 1878, Volume III, page 419, the same authority, 1894, Volume IV, page 774, the fact is stated that ignited titanium oxide Ti_2O_3 and TiO_2 are insoluble in hydrochloric acid.

Fresenius, in his "Treatise on Qualitative Analysis," states that ignited TiO_2 is insoluble in hydrochloric acid.

Prescott and Johnson, in their "Qualitative Analysis," state that metallic titanium is soluble in hydrochloric acid.

As shown by the results of the analysis, there was formed in the pencil made from ilmenite 3.54 per cent. of metallic titanium, this percentage being obtained from the hydrochloric acid solution of the metal. By adding together the percentages of the metallic iron, metallic titanium and the foreign minerals found in the ilmenite pencil, we obtain 74.12 per cent.; the difference between this figure and 100 per cent. is 35.88 per cent, which shows the percentage of the mixed oxides of titanium Ti_2O_3 and TiO_2 present. The percentage of the respective oxides when mixed cannot be determined as there is no method known by which it can be done.

The total titanium found in the ilmenite pencil if calculated as TiO_2 gives 46.53 per cent.; the metallic iron plus the other compounds in the pencil gives 60.58 per cent.; the total of these two percentages is 107.10 per cent. The excess over 100 per cent. shows that the titanium cannot all be present as the higher oxide TiO_2, but must occur in the pencil as part metal and part oxide. If titanium found in the ilmenite pencil were all calculated as the lower oxide Ti_2O_3, this oxide would be present in the amount of 41.87 per cent., which added to 60.58 per cent., the sum of the percentages of iron and the other compounds, would give 102.45 per cent., which still shows an excess of oxygen, indicating that the titanium is present in the ilmenite partly as metal and in part as oxide.

Corroborating this theoretical deduction is the fact that 3.54 per cent. of metallic titanium was found by direct determination.

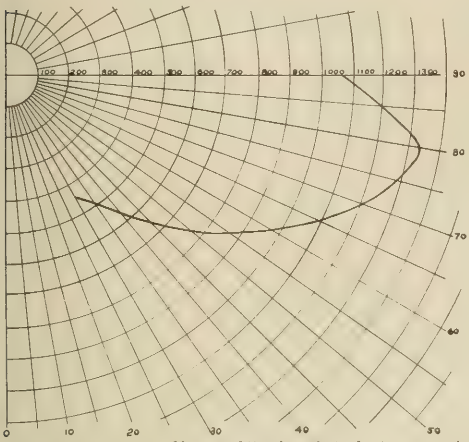


Fig. 5.—Rousseau curve of improved titanium electrode at 5 amp. and 75 volts across the arc.

In the rutile pencil by the same method of calculation, I find that the sum of the percentages of metallic iron and compounds, other than titanium, is 59.14 per cent.; in adding to this the titanium found calculated as higher oxide TiO_2, namely, 48.45 per cent., the sum 107.59 per cent. is obtained, indicating again an excess of oxygen. If the titanium is all calculated as lower oxide Ti_2O_3, we get 43.60 per cent. of Ti_2O_3, which, added to 59.14 per cent., gives 102.74 per cent., a result which still shows an excess of oxygen. As stated above, this indicated excess of oxygen shows that the titanium cannot all be present in the form of oxides. Corroborating this theoretical conclusion is the fact that 3.24 per cent. metallic titanium was found by direct determination.

The metallic iron present in the pencil was determined directly by solution in dilute sulphuric acid with exclusion of air subsequent titration with permanganate of potash, the result showing 45.00 per cent. of metallic iron.

The metallic titanium was determined directly by solution in hydrochloric acid. The result showed 5.22 per cent.

The sum of the metallic iron percentages, namely, 45.00, and the gangue constituents is 59.04 per cent.; if to this is added the titanium found, all calculated as higher oxide TiO_2, we get 102.84 per cent., the excess of oxygen indicating again the reduction of the titanium which is corroborated by the metal found on direct determination.

The metallic iron and metallic titanium were each determined as previously described, the iron showing 45.40 per cent. and the metallic titanium 5.00 per cent.

The sum of the percentages of metallic iron and gangue matter is 60.92 per cent.; upon adding to this figure the percentage of titanium found, all calculated as higher oxide TiO_2 we get 102.32. The excess of oxygen again indicates the presence of metallic titanium, which is corroborated by the metallic titanium found on direct test, namely, 3.00 per cent.

The pencil made from the reduced ilmenite pellets shows metallic iron 50.60 per cent. and metallic titanium 5.64 per cent. The sum of the metallic iron and gangue matter percentages is 62.85; when to this is added the titanium found calculated to higher oxide TiO_2, the figure 105.90 is obtained. The excess of oxygen again indicated the presence of metallic titanium, which is corroborated by the metallic titanium found on direct determination. The conclusion was forced upon the author:

First.—That there was actually a reduction of titanic acid into metallic titanium along with the reduction of the oxygen compounds of iron taking place under the conditions of the manufacture of arc light pencils as above described.

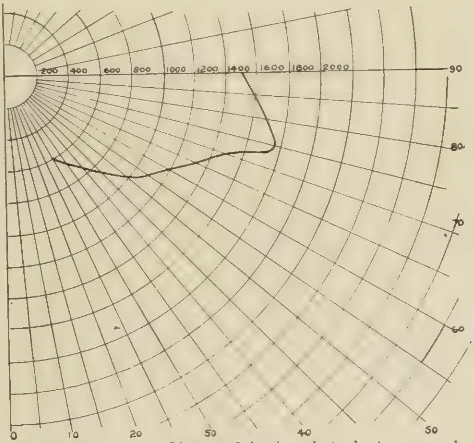


Fig. 6.—Rousseau curve of improved titanium electrode at 5 amp. and 75 volts across the arc.

Second.—That the process of reduction to which the raw material, out of which the arc light pencils were manufactured, led to a storing up of energy

in the arc light pencils. The oxides reduced by the above-described process to the metallic state were then again oxidized in the arc to their previous condition. These processes of oxidation supplied the pencils with the heat necessary for the ionization that caused the selective radiation and luminosity of the arc.

This storing up of energy is the principal distinctive feature differentiating the metallic rutile pencil from the mere conglomeration of the oxygen compounds of iron with oxygen compounds of titanium known under the name of magnetite arc light pencils now on the market. Consequently the author considers himself justified in claiming that his arc light pencil prepared of a mixture of oxygen compounds of iron and titanium, subjected to a process of reduction, are actually ferrotitanium pencils, inasmuch as they contain the metallic titanium and metallic iron, conglomerated and intermingled with each other in one solid cylindrical body.

In order to verify the above formulated conclusion, another electrode, made as above described, was analyzed with the following results:

	Per cent.
Metallic iron	64.89
Oxides of titanium	26.69 (by diff.)
Silica	1.99
Metallic titanium	1.82
Alumina	1.08
Magnesia	1.08
Lime	0.80
Alkalies	0.75
Manganese	0.50
Carbon	0.32
Sulphur	0.08
Phosphorus	Trace
Chromium	None
Metallic titanium soluble in hydrochloric acid	1.86

This pencil contains 3.60 per cent. of a 50 per cent. ferro-titanium, assuming that the alloy of iron and titanium exists here in the proportion of one part of metallic titanium to one part of metallic iron.

The reason for a lower percentage of metallic titanium in this pencil than that found in the pencil reported a year ago, is that in the former pencils there was present a total of about 45 per cent. of titanium calculated as titanic acid, whereas in this pencil there is present a total of only 29 per cent. of titanium calculated as titanic acid. The presence of iron in metallic state is demonstrated beyond doubt and the fact that titanium was obtained in solution by treatment with hydrochloric acid shows, according to recognized authorities in chemistry, that metallic titanium is also present.

Report of Life Tests of Improved Titanium Electrodes. Duration of Each Test 100 Hours.

Pencil E_3—5/8" diam. × 8" long:	
1	57.14
2	43.23
3	43.96
Average hours per inch	48.11
Pencil D_3—9/16" diam. × 8" long.	
1	53.33
2	44.44
3	44.83
Average hours per inch	47.53
Pencil E_3—9/32" diam. × 8" long.	
1	50.00
2	30.76
3	37.18
Average hours per inch	39.31
Pencil E_3—5/8" diam. × 8" long.	
1	57.14
2	43.23
3	43.96
Average hours per inch	48.11

Comparative data as to the life of the improved titanium arc light electrodes and carbon electrodes (at their respective normal current density per square mm.):

	Cm. per one hour.
Life of the D titanium pencil 9/16 in d.	0.075
Life of the averaged cored carbon	1.300
Life of the solid carbon	1.450
Life of the enclosed carbon	0.152
Life of the flaming carbon	3.00
Life of the Bremer type carbon	4.00
Life of the Blondel type carbon	2.00

The increased life of the titanium pencil in hours per inch in comparison with the following carbons, is:

Cored carbons	17.35 times.
Solid carbons	19.33 "
Enclosed carbons	2.03 "
Flaming carbons	40.00 "
Bremer type carbons	53.33 "
Blondel type carbons	26.67 "

Comparative specific resistivity of the titanium arc light electrode and various carbon electrodes (1 m. long, 1 mm.² in diameter):

		Ohms.
Solid carbons.	Brand Conradty C	69.0
Solid carbons.	Brand Henrion (Nancy)	69.0
Solid carbons.	Brand Plania	79.0
Average		72.3
Cored carbons	Brand Siemence A.	72.0
Cored carbons.	Brand Plania	81.0
Average		76.5
Enclosed lamp carbons	Brand Plania, solid	81.0
Enclosed lamp carbons	Brand Eos, solid	89.0
Average		85.0

	Ohms.
Bremer type carbons. Brand Plania, white.....	84.0
Bremer type carbons Brand Plania, with nickel-plating............................	58.0
Bremer type carbons. Brand Plania Rosa......	88.0
Bremer type carbons. Brand, Plania, yellow....	87.0
Bremer type carbons. Brand Siemence, white..	93.0
Bremer type carbons. Brand Siemence, yellow..	106.0
Bremer type carbons. Brand Siemence, yellow, with copper-plating....................	29.3
Bremer type carbons Brand Siemence Conradty Noris, yellow, with copper plating ...	60.5
Same, with wire in the core	81.0
Siemence, yellow, with metallic wire in the core..	39.0
Average..................................	72.58

The resistivity of the titanium pencil is 2.02 ohms. Consequently:

The resistivity of the average solid carbon pencil is 36 times.

The resistivity of the average cored carbon pencil is 38.25 times.

The resistivity of the average enclosed carbon pencil is 42.5 times.

The resistivity of the average Bremer type carbon is 36.2 times that of the titanium pencil.

[From the Rudolph Spreckels Physiological Laboratory of the University of California.]

A RAPID METHOD OF DETERMINING THE PERCENTAGE OF CASEIN IN MILK.

By T. Brailsford Robertson

Received May 10, 1909.

In a recent paper[1] I have shown that the difference between the refractive indices of two solutions of a caseinate, which differ only in their casein-content, is proportional to the difference between the percentages of casein which they contain; in other words, that

$$n - n_1 = a \times c,$$

where n is the observed refractive index of the solution, c is the percentage of casein which it contains, n_1 is a constant, the value of which depends upon the concentration and nature of the alkaline (or acid) solution employed as solvent, and a is a constant numerically equal to the change in the refractive index of the solvent which is brought about by the addition to 100 cc. of 1 gram of casein. I have also shown that by means of the above formula the concentration of casein in a solution can be very accurately determined, the deviations from accuracy rarely exceeding 2 per cent. of the quantity of casein contained in 100 cc. of the solution (provided that quantity exceeds 0.5 gram) and that the change in the refractive index of a given volume of a solution of a base which is brought about by the introduction of a given weight of casein is independent of the concentration of the base and of the nature of the base; if the volume be 100 cc. and the weight of casein 1 gram, the change in the refractive index is 0.00152.

It occurred to me that these facts might be applied to the determination of the percentage of casein contained in fluids such as milk.[1] The procedure of the determination was as follows:

Fifty cc. of fresh, unskimmed milk were diluted to 250 cc. and 75 cc. of $N/10$ acetic acid (made up by diluting 10 cc. of glacial acetic acid to 1750 cc.) were slowly added, the mixture being continuously and rapidly stirred during the addition. The precipitate was then allowed to settle and the supernatant fluid was poured through a 15 cm. S. & S. No. 589 "white band" paper. The precipitate was then washed by decantation with distilled water several times, the washings, and, subsequently, the precipitate being transferred to the same filter. The filter and precipitate were then allowed to drain for about 1 hour and were then transferred to a dry beaker and 100 cc. (accurately measured) of $N/10$ NaOH were added and the filter and precipitate were macerated (by the aid of a stirring rod protected at the tip by rubber) until the filter paper was transformed into a fine pulp and the casein was completely dissolved. As the casein particles are of a different color to the particles of paper, the point of complete solution can be readily determined; complete solution of the amounts dealt with in this determination is usually attained within ten minutes. The mixture was then filtered[2] and the refractive index of the filtrate determined, by means of a Pulfrich refractometer reading accurately to within 1′ of the angle of total reflection, if possible at 20° C. Since n for $N/10$ NaOH is 1.33444 (at 20° C.),[3] the results are calculated as follows:

$$\text{Grams casein in 50 cc. milk} = \frac{n - 1.33444}{0.00152}$$

where n is the refractive index of the final solution, obtained as described above.

An obvious source of error is the water associated with the precipitate and filter paper when they are transferred to the $N/10$ NaOH. As the succeeding determinations show, however, with the

[1] T. Brailsford Robertson: *Journ. of Physical Chem.*, **13**, 469 (1909).

[1] Since writing the above, I have found that Reiss (*Arch. f. Exper. Pathol. und Pharm.*, **51**, 18 (1903), *Beitr. z. chem. Physiol. und Pathol.*, **4**, 150 (1904)) has previously employed the refractive indices of body-fluids as a measure of their protein-content.

[2] This filtration can be omitted provided the solution be allowed to stand for a sufficient time so that the particles of paper settle to the bottom of the beaker.

[3] Cf. the paper cited above.

amounts of casein likely to be obtained from 50 cc. of milk, and provided the precipitate is allowed to drain for a sufficient time this error is, for all practical purposes, negligible. It could, of course, be eliminated, if desired by diluting the final solution, before filtration, to an accurately measured volume with $N/10$ NaOH; in that case it would be advisable to start with 100 cc. of milk instead of 50 cc., completely dissolve the precipitate in 100 cc. of $N/10$ NaOH and then make up the volume of the mixture to 200 cc. by the addition of N/10 NaOH. The slight dilution of the *sodium hydroxide* caused by this procedure does not affect the accuracy of the determination, since the refractive index of a dilute sodium hydrate solution varies very much less with its concentration than that of a solution of casein of the concentrations employed above.

For comparison, determinations were carried out by the official method[1] as follows:

Twenty cc. of fresh unskimmed milk were diluted to 100 cc. and 30 cc. of $N/10$ acetic acid were slowly added, the mixture being continuously and rapidly stirred during the addition. The precipitate was then allowed to settle and the supernatant fluid was poured through a 15 cm. S. & S. No. 589 "white band" paper. The precipitate was then washed by decantation with distilled water several times, the washings, and, subsequently, the precipitate being transferred to the same paper. The filter and precipitate were then digested with 20 cc. of H_2SO_4, to which a trace of metallic mercury had been added, as in the ordinary Kjeldahl method for the determination of nitrogen, and the process of determining the nitrogen was completed by the official Kjeldahl method. The number of grams of casein in the 20 cc. of milk was estimated by multiplying the number of grams of nitrogen thus determined by 6.25.

Four determinations by the new method yielded the following results:

	Grams casein in 100 cc. milk
a	2.84
b	2.84
c	2.84
d	2.84
Average	2.84

Four determinations by the official method, using the same milk, yielded the following results:

	Grams casein in 100 cc. milk.
a	2.69
b	2.81
c	2.78
d	2.69
Average	2.74

The agreement is sufficiently satisfactory. The factor 6.25 by which the nitrogen is multiplied to obtain the equivalent in casein is calculated on the assumption that the percentage of nitrogen in casein is 16. If, however, we take 15.65 as the true percentage of nitrogen in casein, which, according to the results of Hammersten,[1] Lehmann and Hempel,[2] and Ellenberger,[3] would appear to be the more accurate figure, then the factor by which nitrogen is multiplied becomes 6.4 and the agreement between the official and the new methods is even more satisfactory, the above four determinations by the official method yielding the results:

	Grams casein in 100 cc. milk.
a	2.75
b	2.88
c	2.85
d	2.75
Average	2.81

In order to further test the accuracy of the method, weighed amounts of casein were dissolved each in 100 cc. of $N/50$ NaOH and were precipitated, with constant stirring, by the addition of 30 cc. of $N/10$ acetic acid. The casein employed in these experiments was the c. p. product manufactured by Eimer & Amend and further purified by trituration with large volumes of distilled water alcohol (absolute) and ether (ueber natrium dist.); it was dried for 24 hours at 36°. The properties of the product thus obtained have been fully described by me in a previous paper;[4] it gives every indication of being a pure product, being insoluble in distilled water (save in traces which adhere to the undissolved particles) and completely precipitated by acetic acid. It neutralizes to phenolphthalein exactly the quantity of base determined by Laqueur and Sackur and by Van Slyke and Hart;[5] it is free from appreciable water. The first

[1] *U. S. Department of Agriculture, Division of Chemistry Bulletin* **46**, Revised Edition (1899), p. 55. The details of the precipitation were slightly modified and the quantity of milk employed in the determination was double that recommended by the Association of Official Agricultural Chemists.

[1] O. Hammersten, *Zeitschr. f. Physiol. Chem.*, **7**, 227 (1883); **9**, 273 (1885).

[2] W. Hempel, *Arch. f. d. ges. Physiol.*, **56**, 558 (1894).

[3] Ellenberger, *Arch. f. Anat. und Physiol., Physiol. Abt. Suppl.*, p. 313 (1902).

[4] T. Brailsford Robertson, *Journ. of Biol. Chem.*, **2**, 317 (1907).

[5] Laqueur and Sackur, *Beitr. z. Chem. Physiol. u. Path.*, **3**, 193 (1902). Van Slyke and Hart, *Amer. Chem. Journ.*, **33**, 461 (1905).

two determinations were carried out in exactly the same manner as those of the casein in milk, described above. The last three, in which larger quantities of casein were determined, were determined in the same manner save that the final solution, before filtration, was diluted to 250 cc. (accurately measured) so as to eliminate the error due to water associated with the precipitate and paper. The results follow:

Grams casein in 100 cc. solution.

Weighed.	Determined.
1.0	1.02
2.0	1.88
3.0	2.90
4.0	3.88
5.0	5.03

The agreement is as close as could be desired.

If the refractive index of the final solution be determined at temperatures above 20° and below 30°, 0.0001 must be subtracted from the value of the constant n_1 (= 1.33444 at 20° when the solvent is $N/10$ NaOH) for every degree by which the temperature exceeds 20°. If it be determined at temperatures below 20° and above 10° 0.00007 must be added to the value of the constant n_1 for every degree by which the temperature is less than 20°.[1]

The advantages of the method herein described over the official method for the determination of casein are manifest. Not only is the time consumed in the determination much reduced, the time actually occupied in manipulation, exclusive of that allowed for drainage of the precipitate, being not much over 1/2 hour, but the whole procedure is much simplified and the accuracy of the determination is unimpaired.

For further details concerning the dependence of the refractive index of casein solutions upon their concentration, the nature of the solvent, the temperature, etc., I must refer the reader to my previous paper, cited above.

[1] Cf. my previous paper, referred to above.

[Contribution from the Department of Agricultural Chemistry, University of Missouri.]

CHANGES IN THE COMPOSITION OF THE SKELETON OF BEEF ANIMALS.

(FIRST PAPER.)

By P. F. Trowbridge and F. W. Woodman.

Received July 1, 1909.

The study of the composition of the skeletons of beef animals reported in this paper constitutes a portion of the general study of the "Uses to which the Animal Puts Its Food," now in progress in the Experiment Station of the University of Missouri. In the work during the past two years, fifteen animals have been slaughtered and analyzed. Of these the six mentioned in this paper were used chiefly to study the resorption of fat which takes place when an animal in good condition of nourishment is unable to obtain a usual food supply. Only the skeleton is considered in this paper.

The housekeeper regards the skeleton as merely so much waste material. To the animal husbandman it is of very great importance, determining, to a large extent, the size and value of the animal. To him an exact knowledge of the conditions of growth of the skeleton and to what extent it is affected by adverse conditions is very important.

Lawes and Gilbert, in their classic researches at Rothamsted, made a special study of the ash content of the carcasses of beeves and other animals. They pointed out especially the variation of the proportion of mineral matter in the bones to that in all other parts of the body, dependent upon the degree of fatness of the animal.

Wildt,[1] working with rabbits, made a special study of the effect of age on the chemical composition of the skeleton of young and of full-grown animals. He concluded that age had little effect after the animal had reached full growth, the composition of the skeleton varying with the condition of the animal. Mann[2] drew the same conclusions, though from rather indefinite data.

Düring[3] gives tables showing the difference in composition of the bones of various parts of birds. He showed that the composition of the air-dry bone varies in different parts of the skeleton.

Brookman[4] made comparative analyses of the skeletons of cow, sheep, horse and swine.

Gabriel[5] studied especially the methods of analysis of bones. His investigation of the composition of the bone ash was very thorough and he gives a probable composition of bone ash.

The phosphorus in the marrow is largely in organic form, according to Otolsky.[6] He found 0.13 per cent. to 0.15 per cent. lecithin in the marrow of the leg bones of the horse. W. Gliken[7] obtained similar results with both human and animal skele-

[1] *Landw. Versuchsst.*, **15**, 404 (1872).
[2] *Chem. News*, **51**, 132 (1887).
[3] *Zeit. physiol. Chem.*, **7**, 446 (1883).
[4] *Ber.*, 388 (1882).
[5] *Zeit. physiol. Chem.*, **19**, 257 (1894).
[6] *Abs. in Jahresb. u. Tier. Chem.*, **37** (1908).
[7] *Biochem Ztschr.*, **4**, 235 (1908).

tons. He also found that the per cent. of lecithin in the marrow decreases with age.

The effect of nourishment upon the skeleton has been studied extensively, the investigations following three general lines: (1) the effect of feeding rations normal in other respects, but poor in one or more necessary mineral constituents; (2) the comparative effect of organic and inorganic compounds as sources of phosphorus; (3) the effect of starvation upon the composition and weight of the skeleton. The results of the various investigators[1] seems to show: Foods poor in calcium have little effect upon the skeleton. Foods low in phosphorus have a pronounced effect, producing weakness, brittleness and actual loss in weight of the skeleton.

Whether the form of combination of the phosphorus has any effect is still disputed.

Inanition decreases the fat and increases the moisture in the skeleton but does not appear to effect the mineral composition to any noticeable extent.

EXPERIMENTAL PART.

Objects of this Investigation.

In the investigations noted above the variations in the kind and conditions of the animals used, the object and methods of the work, and the varying manner of reporting make it hard to compare the results. In the course of the series of experiments upon the effect of breed, feed and age upon the composition of animal flesh, and the distribution of the food materials in the various parts of the animal body, which investigations are being carried on at the Missouri Agricultural Experiment Station, it became desirable to know the composition of the skeleton of the animals under consideration. With this object in view, the following work was undertaken, having special reference to the distribution of phosphorus in the different parts of the skeleton.

Condition and Age of Steers at Time of Slaughtering.

The six steers reported in this paper were all from the group known as "special maintenance steers." They were from the same sire and herd of cattle, grade Herefords; of about the same age, spring calves of 1907, and had run on grass until purchased for the experiment in fall of 1907. At the outset all were put upon full feed, consisting of 2.5 parts grain (composed of 8 parts corn to 1 linseed meal) to one part alfalfa hay, until in nearly prime condition.

In February, 1908, steer 594 was killed as a check animal. He was a fat yearling, showing Shorthorn blood, and was in a nearly finished condition. His carcass graded as "baby beef."

Steers 591, 593 and 597 were killed in September, 1908, after having been kept on "special maintenance" for six months.

Steer 591 was eighteen months old when killed, and had been kept on "submaintenance" for six months, being made to lose one-half pound daily. He was very thin, his carcass being graded as a "canner."

Steer 597 was eighteen months old when slaughtered. He had been kept on "maintenance," being kept at the same weight, neither gaining or losing. His carcass graded as No. 3 beef, being too thin for No. 2.

Steer 593 had been kept on "supermaintenance" for six months, being made to gain one-half pound per day. He was eighteen months old when slaughtered and graded as No. 2 beef

Steer 592 was killed in January, 1909, being about 22 months old when killed. He had been kept on "submaintenance" for eleven months, was exceedingly thin and graded as a "poor canner." The appearance of the skeleton of this steer was remarkable, the marrow having nearly all disappeared, and in its place was a watery, ill-smelling liquid, having none of the ordinary properties of normal marrow, and no greasy or fatty appearance whatever.

Steer 595 was slaughtered in February, 1909, after having been kept on "maintenance" for a year. He was graded as a "canner."

The feed of all these animals was exactly the same in quality, differing only in quantity from the beginning, so that whatever differences appear in the skeleton are due to amount of food and individuality of the animals.

Method of Obtaining Samples.

The samples were obtained at the time of slaughtering and when the carcass was cut up, forty-eight hours later. The carcass of each animal was cut into the regular wholesale cuts, and the right

[1] Weiske, *Zeit. physiol. Chem.*, **20,** 595 (1895). Lehman *Jahresb. u. Agr. Chem.*, **20,** 382 (1877). Sedlmair, *Zeit. f. Biol.*, **37,** 25 (1898). Gusmitta *Jahresb. u. Thier Chem.*, **1884,** 401. Forbes *Bull.* **201** (1909), *Ohio Agr. Expt. Station.* Wiley, "Composition of Carcass of Pigs," *U. S. Dept. Agr., Division of Chemistry, Bull.* **53,** page 70 (1898). Hart, McCullum and Fuller, *Am. Jour. Physiol.*, **23,** 246 (1909). Hart, McCullum and Humphrey, *Ibid.*, **24,** 86 (1909).

half taken for all chemical analyses, being hand-separated into lean, fat and bone.

The bone samples were made up for analysis as follows: (1) head and tail; (2) feet minus hoofs; (3) shin and shank; (4) chuck and neck; (5) flank and plate; (6) ribs; (7) rump; (8) loin; and (9) round. The reasons for combining the samples in pairs in some cases was to reduce the number of samples.

The whole bone was taken for analysis, including such adhering fat, lean and tendon as could not be removed with a knife. The bones were not boiled nor heated to remove the adhering flesh in any case. The marrow was thus included in the sample.

In the case of 594, the bones of the various cuts were not analyzed separately, but a composite of the whole was made and analyzed as one sample. The analysis of this animal will therefore be comparable only with the averages of the others.

METHODS OF ANALYSIS.

Preparation of Sample for Analysis.

As the samples of bone were removed from the carcass they were weighed quickly to avoid loss of moisture, then broken up, and ground in a Mann's bone grinder. The ground sample was mixed thoroughly and quartered down to the desired size of sample. This portion was put into closed jars and sent at once to the laboratory or kept in the cooler until it could be weighed out for analysis.

Moisture.

Samples for moisture and fat were weighed out rapidly, in triplicate, in tared porcelain evaporating dishes, the size of the sample varying according to the fat content, as judged by the appearance of the bone. For fat, greasy samples, 25–40 grams were considered sufficient while for those with little fat 100 grams or even more were sometimes taken.

The dishes containing the weighed samples were at once placed in vacuum desiccators and dried over sulphuric acid, at room temperature, by means of the Benedict vacuum method, as modified for use in this laboratory.[1]

This method has proved very satisfactory, agreeing very closely with the older methods, and leaving the sample in perfect conditions for further analyses.

[1] P. F. Trowbridge (Nov. 1908). Proceedings of the Association of Official Agricultural Chemists (*U. S. Dept. of Agriculture, Bureau of Chemistry, Bull.* **122**). L. F. Shackell, *Am. Jour. Physiol.*, **24**, 325 (June, 1909).

Fat.

The determination of fat was made upon the same samples as for moisture. The dry substance was transferred carefully to Soxhlet extractors prepared by placing a pad of absorbent cotton in the bottom to filter the ether extract.

Redistilled anhydrous ether was used for the extraction, the fat being collected in tared flasks and weighed after drying for 24 hours in vacuum

After drying and extraction the triplicate samples were combined in one and ground in a steel mill until fine enough to pass through a millimeter mesh sieve. This ground, air-dry sample was used for the determination of ash and phosphorus.

Ash.

Two gram samples were weighed out in tared porcelain crucibles dried at 100–110°, and the moisture determined. The samples were ashed by igniting over bunsen burners until practically free from carbon, the ignition being completed in the muffle at dull red heat. A clear, white ash could be readily obtained by this means in a short time.

Phosphorus.

The ash from the above determination was dissolved by digestion in hot, dilute nitric acid and the solution made up to 250 cc. Aliquots of 25 cc. were taken and the phosphorus determined gravimetrically as in fertilizers by the official methods of the Association of Official Agricultural Chemists (*U. S. Dept. Agr., Bureau of Chem., Bull.* **107** (revised).

DISCUSSION OF THE RESULTS.

In an investigation conducted, as this one was, with animals which must of necessity differ in many characteristics, much depends upon selecting animals which are as nearly alike in all respects as it is possible to obtain them. The steers in the "special maintenance" group, of which these six steers were a part, were all selected with the greatest care to obtain animals of the same age, size, breed, and general condition. However, even after this careful selection there were individual characteristics which influenced the results, especially the weight and proportion of the skeleton.

The weights of the skeleton as shown in Tables I and II are almost solely a matter of the individual characteristics of the animals. No. 594, killed at the outset, was the smallest of all the steers and the total weight of his skeleton is also the smallest. Measurements made during the feeding period show that the special maintenance steers all con-

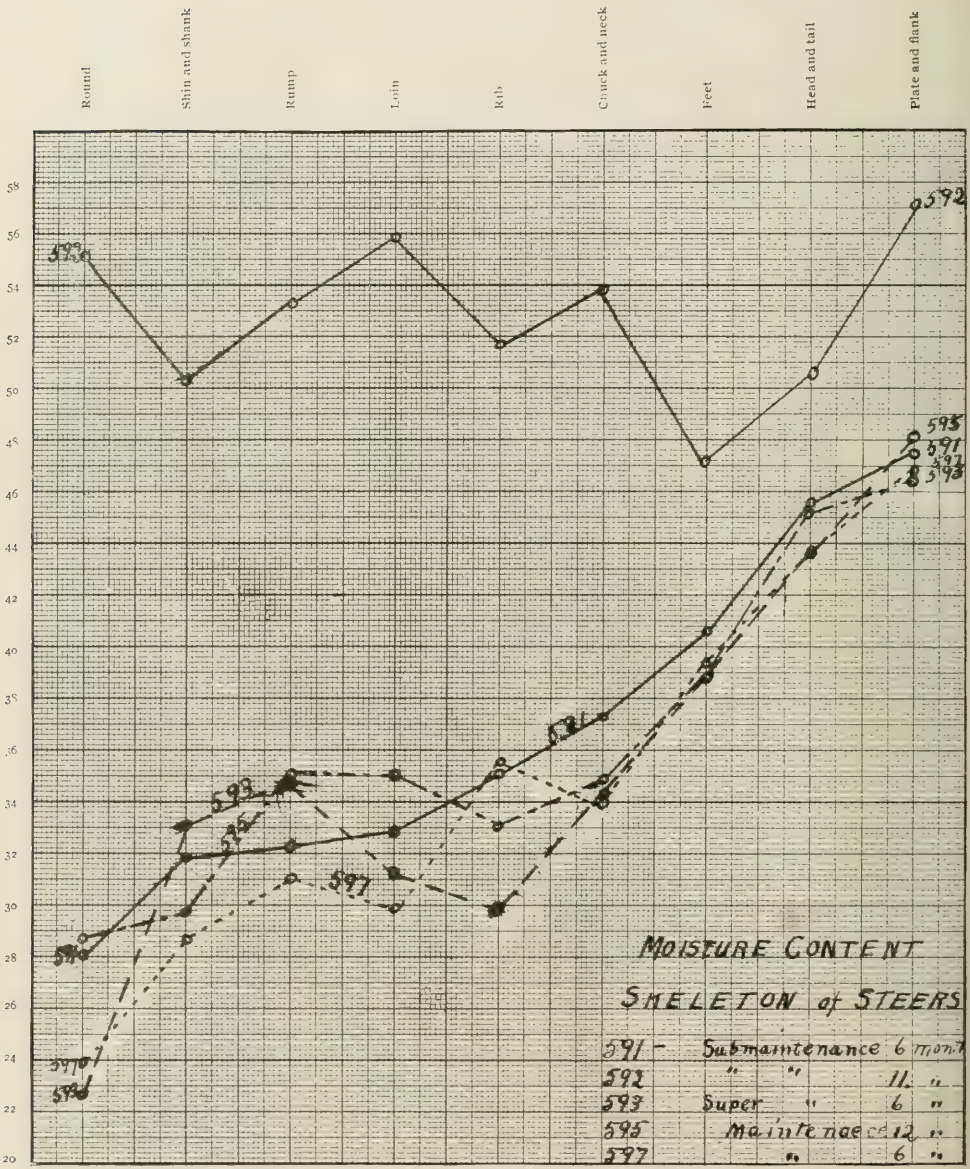

Round
Shin and shank
Rump
Loin
Rib
Chuck and neck
Feet
Head and tail
Plate and flank
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
592
593
595
591
597
MOISTURE CONTENT
SKELETON of STEERS
591 - Submaintenance 6 mont
592 " " 11 "
593 Super " 6 "
595 Maintenance 12 "
597 " 6 "

Plate 1.

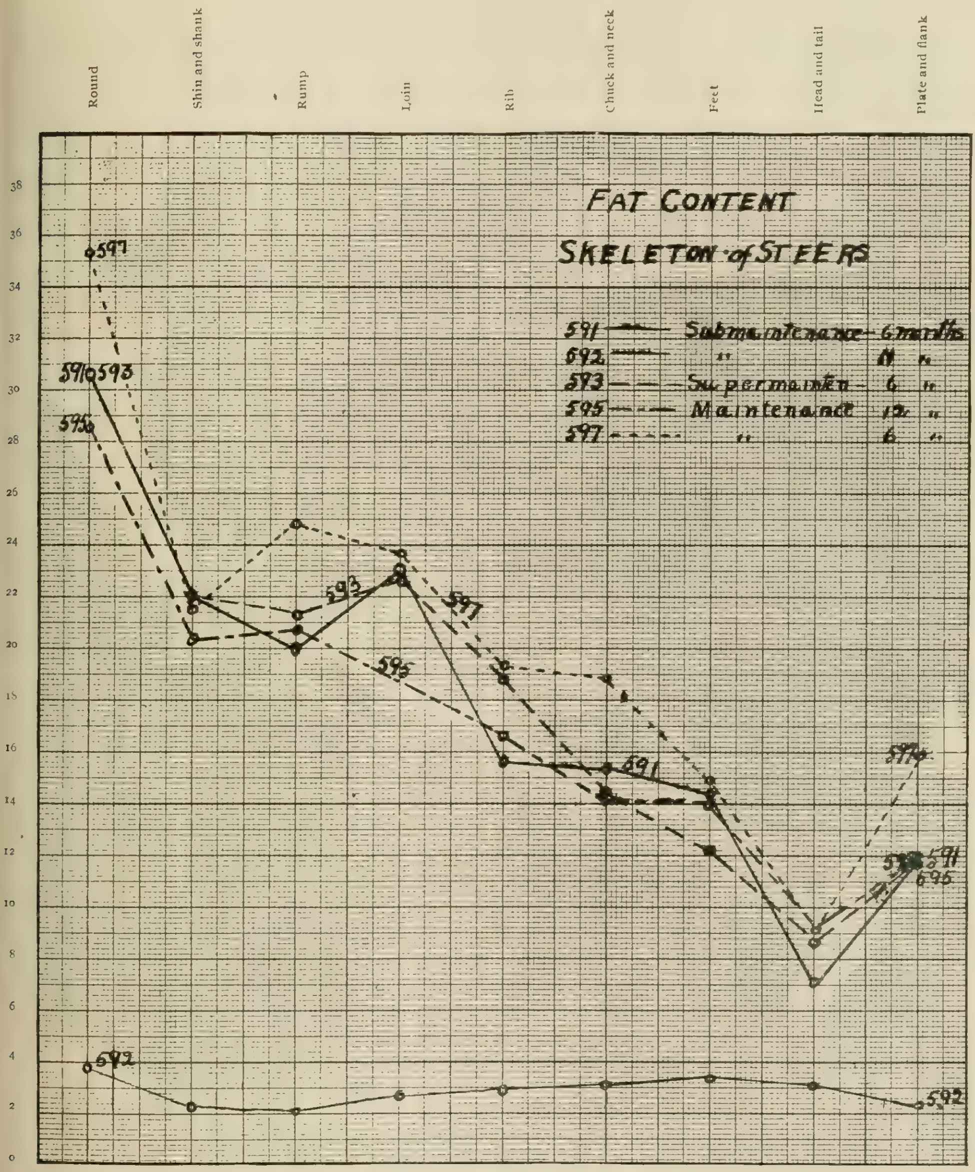

Round
Shin and shank
Rump
Loin
Rib
Chuck and neck
Feet
Head and tail
Plate and flank
FAT CONTENT
SKELETON of STEERS
591 Submaintenance 6 months
592 " 11 "
593 Supermainten 6 "
595 Maintenance 12 "
597 " 6 "
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0

Plate 2.

tinued to grow in height, those on maintenance and submaintenance, as well as the supermaintenance animals, indicating that the animal continues to build up the skeleton even when insufficient food is supplied for maintenance. The total weight of the skeleton is higher in all of the older steers than in 594, the young animal killed as a check. The difference is only slight in the case of 591. Steers 593 and 597 were very much alike in empty weight and weight of skeleton, though in physical condition, before slaughtering 593, was considerably superior to 597.

Steer 597 was, in some respects, unlike the other two animals killed in September, being not only larger but also coarser boned. The skeleton of this animal shows a higher fat content and a correspondingly lower moisture content than does that of 593, the former having been on maintenance for six months and the latter on supermaintenance for the same length of time (Tables III and IV).

The ratio of weight of skeleton to the empty weight of the animal varied with the condition of the animal at slaughtering (Table I). The term "empty weight" meaning the live weight of the animal minus the contents of the digestive and excretory system.

Moisture and Fat.

The moisture and fat content of the skeleton of each animal is shown in Tables III and IV. The check steer, 594, was low in fat and high in moisture content, as compared with the other four animals, 591, 593 595 and 597. This can be accounted for by the age of the animal, Wildt[1] and others having shown that the fat content of the skeleton in growing animals increases with age. The four steers named above were, apparently, so fat as moisture and at content of the skeleton is concerned, normal animals. The variations between the different steers was in no case greater than could be explained by individuality.

The extreme effect of poor nutrition was shown in 592. The condition of this animal was approaching that of starvation. Practically all the fatty tissue had disappeared from his muscles, and even the marrow had gone. This is proved by the extremely low per cent. of fat in the skeleton, 3.09 per cent., as contrasted to that of the others, which averaged 17.09 per cent. The moisture content of the skeleton of 592, 52.46 per cent., contrasts as sharply with the average for the other five steers, 36.54 per cent.

[1] Landwirts, Versuchs Stationen. **15**, 404 (1872

Steer 595, after being on maintenance for a year, illustrated an important point sought in this investigation. This animal had continued to grow in size while remaining constant in weight. The growth had been at the expense of the fat in the muscles and tissues of the body, and when slaughtered almost no fat could be separated by hand from the muscles. At the same time the fat content of the bones was only very little, if at all, below that of normally fed animals. It is thus seen that the poorly nourished animal resorbed practically all of the fat from the muscles and tissues of his body before drawing upon the fat contained in the skeleton.

The distribution of the fat and water in the individual animals is shown also in Plates 1*a* and 1*b*. In the plates the cuts are so arranged as to give an ascending curve for one animal, steer 591 being taken as the basal animal. The arrangement of the cuts of this steer to give an ascending curve for the moisture content of the separate cuts gives a similar curve for the other steers, with the exception of 592. The variation in the moisture tent is not uniform in all cases, single cuts of each animal deviating from the general curve, but in general the order is the same for all of the four steers.

The fat curve is almost an exact reverse of that for moisture, the only general exception being in the case of the flank and plate cut. This cut containing more cartilage is highest of all in moisture, but also contains a fairly high per cent. of fat.

Steer 592 shows a striking exception in the distribution of moisture in the different cuts of the skeleton. The moisture curve for this animal instead of being a rapidly ascending curve is an irregular line having no semblance to the curve of the other animals. The curve representing the fat content of this animal is a comparatively horizontal line, with an extreme variation of less than two per cent. This shows that in the struggle to maintain life this steer had resorbed nearly all the marrow, until he had reached the extreme, where all portions of his skeleton contained practically the same amount of fat, averaging 3.09 per cent. of the whole weight of the skeleton.

The figures obtained by adding the per cent. of moisture to that of fat vary widely in the different parts of the skeleton of each animal, according to the nature of the bone in the cut. The variation is not constant in the different animals, and could not be plotted to show any similarity in curves.

The sum of the per cents. of moisture and fat is, however, nearly the same for the composite of the whole skeleton in all of the animals as shown in Table I. The fact that in steer 592 the sum of the moisture and fat in the skeleton is a little higher than in the other steers indicates that when fat is resorbed water is deposited in its place, and the reverse may very probably be true during the fattening of animals and may explain why a steer may be getting fat but not gaining weight.

TABLE I.

SUMMARY OF COMPOSITION OF SKELETON OF SIX SPECIAL MAINTENANCE STEERS.

	Weight of skeleton, kilos.	Empty weight of steers, kilos.	Per cent. skeleton to empty weight.	Moisture in skeleton. Per cent.	Ether-soluble (fat) in skeleton. Per cent.	Sum of moisture and fat in skeleton. Per cent.	Ash in skeleton Per cent.	Phosphorus in ash of skeleton. Per cent.	Phosphorus in skeleton. Per cent.	Ash in skeleton freed from moisture and fat. Per cent.	Phosphorus in skeleton freed from moisture and fat Per cent.	Organic matter in skeleton not fat. Per cent.	Remarks.
Steer No. 594	39.270	247.52	15.86	39.89	14.68	54.57	23.81	18.48	4.40	52.40	9.11	21.63	Slaughtered as check animal, Feb., 1908
Steer No. 593	51.104	317.92	16.07	35.36	17.63	52.99	25.29	18.15	4.59	53.81	9.77	21.72	Six months supermaintenance, slaughtered, Sept., 1908
Steer No. 597	51.012	302.56	16.86	34.32	19.53	53.85	24.72	18.65	4.61	53.57	9.99	21.43	Six months maintenance, slaughtered, Sept., 1908
Steer No. 595	44.912	230.24	19.51	36.11	16.47	52.58	26.42	18.89	4.99	55.72	10.53	21.00	One year maintenance, slaughtered, Feb., 1909
Steer No. 591	40.396	190.31	21.22	37.02	17.32	54.34	23.81	18.45	4.39	52.15	9.62	21.85	Six months submaintenance, slaughtered, Sept., 1908
Steer No. 592	48.430	190.20	25.46	52.46	3.09	55.55	22.76	18.29	4.16	51.19	9.37	21.68	Eleven months submaintenance, slaughtered, Jan., 1909

Organic Matter not Fat.

The organic matter other than fat was calculated for the individual cuts of each animal, and it seems to be practically constant for all animals, varying in the cuts calculated between the limits 20.5 per cent. and 22.5 per cent. in the different parts of the same steers. For the composite of each of the six animals this content of organic matter, not fat, varied between the limits of 21.00 per cent. and 21.95 per cent., or is practically constant. This was calculated by difference, being the loss on ignition of the dry and fat-free substance. The constant proportion of this organic matter which forms the framework of the skeleton shows that in none of the animals was the ratio of the organic portion other than fat changed by feeding during the period. The slight differences in the per cent. of this organic substance are no greater than can be attributed to the variations in sampling or other causes.

Ash.

The ash represents the mineral portion of the skeleton and is a large part of the total weight (Tables I and V). Since, as has been shown, the organic matter other than fat is practically the same for the different animals, the per cent. of ash in the original sample will be of little value, since it will be entirely dependent upon the sum of fat and moisture.

The per cent. of ash in the original sample varied with no regularity in the separate cuts of the individual animals. The only cuts in which all the animals were similar were the flank and plate, which was lowest in ash in all cases, and the head and tail which analyzed very close to 25.00 per cent. of ash in all animals.

TABLE II

WEIGHT OF SKELETON OF THE SEPARATE CUTS, GRAMS

No. of steer	593	597	595	591	592	594
Head	6302	6357	5620	4888	4454	4740
Tail	222	270	280	146	342	146
Feet	5574	5378	4584	4570	5112	4576
Shins	4132	4114	3344	3572	4014	2974
Shanks	4650	4503	4032	3668	4316	3362
Chucks	9259	9820	8006	7248	8906	6890
Neck	756	932	952	796	1112	720
Flanks	63	32	92	80	76	78
Plates	4187	4240	3650	3324	4432	2998
Ribs	4325	4382	4290	3378	5050	3696
Loins	5001	5172	4690	3905	4446	4654
Rumps	2164	1644	1582	1335	1788	1120
Rounds	4470	4168	3790	3516	4380	3312
Total	51105	51012	44912	40396	48430	39266

TABLE III

PER CENT. MOISTURE IN SKELETONS OF SPECIAL MAINTENANCE STEERS.

No. of steer	593	597	595	591	592	...
Head and tail	43.70	43.83	45.12	45.58	50.77	...
Feet	38.58	38.66	39.34	40.55	47.29	...
Shins and shanks	33.31	28.69	29.74	31.94	50.37	..
Chucks and neck	34.24	34.00	34.90	37.33	53.81	...
Flanks and plates	48.19	46.99	46.43	47.46	57.21	.
Ribs	30.86	35.42	33.01	35.12	55.95	. .
Loins	31.20	29.92	35.14	32.87	51.67	..
Rumps	34.86	31.01	34.93	32.84	53.28	...
Rounds	22.71	23.93	28.69	28.10	55.13	...
Total skeleton	35.36	34.32	36.11	37.02	52.46	39.86

The per cent. of ash in the dry and fat-free substance (Table VI) is a better indication of the ash content than the per cent. in the fresh sample.

Steer 595, the oldest of the lot when killed, was highest in ash content, this being not true of all parts of the skeleton, but of the skeleton as a whole.

TABLE IV.

PER CENT. FAT IN SKELETONS OF SPECIAL MAINTENANCE STEERS.

No. of steer	593	597	595	591	592	594
Head and tail	8.68	9.05	9.14	7.18	3.15	
Feet	12.23	14.82	14.03	14.42	3.43	
Shins and shanks	21.92	21.56	20.36	22.03	2.25	
Chucks and neck	14.53	18.91	14.13	15.26	3.13	
Flanks and plates	11.87	15.85	11.95	11.68	2.25	
Ribs	18.79	19.31	16.59	15.56	2.69	
Loins	22.92	23.57	18.74	23.10	2.87	
Rumps	21.30	24.76	20.68	20.09	2.15	
Rounds	30.48	35.29	28.62	30.39	3.81	
Total skeleton	17.63	19.53	16.47	17.32	3.09	14.68

TABLE V.

DISTRIBUTION OF ASH IN SKELETONS OF SPECIAL MAINTENANCE STEERS, EXPRESSED IN PER CENT. OF FRESH WT.

No. of steer	593	597	595	591	592
Head and tail	25.00	25.00	25.61	25.29	25.08
Feet	25.32	23.73	25.78	22.14	24.42
Shins and shanks	24.41	27.81	28.76	24.91	26.28
Chucks and neck	27.42	25.83	28.05	24.23	21.45
Flanks and plates	17.24	15.36	19.63	17.71	17.62
Ribs	27.86	23.69	27.44	26.17	22.36
Loins	24.75	25.81	26.83	23.59	20.66
Rumps	25.94	23.66	24.13	26.20	23.57
Rounds	28.12	24.01	26.03	23.60	22.30
Total skeleton	25.29	24.72	26.42	23.81	22.76

TABLE VI.

PER CENT. OF ASH REFERRED TO SKELETON FREED FROM MOISTURE AND FAT.

No. of steer	593	597	595	591	592	594
Head and tail	52.51	53.07	56.00	53.54	54.36	
Feet	51.48	51.00	55.29	49.19	49.56	
Shins and shanks	54.54	55.91	57.62	54.11	55.47	
Chucks and neck	53.52	54.85	55.03	51.10	49.83	
Flanks and plates	43.17	41.35	46.92	43.34	43.47	
Ribs	55.34	52.33	54.46	53.07	49.20	
Loins	53.95	55.58	58.17	53.59	49.95	
Rumps	58.67	53.50	54.37	55.07	52.90	
Rounds	59.95	58.87	60.98	56.85	54.31	
Total skeleton	53.81	53.57	55.72	52.15	51.19	52.40

TABLE VII.

DISTRIBUTION OF PHOSPHORUS IN SKELETONS OF SPECIAL MAINTENANCE STEERS; IN PER CENT. OF FRESH WEIGHT.

No. of steer	593	597	595	591	592
Head and tail	4.59	4.63	4.99	4.48	4.42
Feet	4.59	4.38	4.72	3.89	4.34
Shins and shanks	4.44	5.21	5.56	4.54	4.90
Chucks and neck	4.89	4.71	5.18	4.75	3.99
Flanks and plates	3.12	3.09	3.63	3.35	3.17
Ribs	5.06	4.47	5.22	4.75	4.11
Loins	4.61	4.84	5.18	4.25	3.82
Rumps	4.32	4.55	4.49	4.68	4.34
Rounds	5.28	4.49	4.83	4.45	4.05
Total skeleton	4.40	4.61	4.99	4.41	4.16

Although steer 592 was the second oldest of the six, the ash content of his skeleton was lowest, in the skeleton as a whole. This may be a mere coincidence or it may point to a resorption of mineral matter from the bones during a long period of insufficient nutrition. No conclusion can be drawn from only one animal. Compare the recent work of Hart[1] and others at the Wisconsin Agricultural Experiment Station.

Phosphorus.

The percentages of phosphorus, reported in Tables I and VII, are those obtained by determination of the phosphorus in the ash.

In order to show that very little phosphorus is dissolved by the ether, determinations of phosphorus were made upon each sample of fat extracted from the skeletons of steers 591, 593 and 597. The results show that the amount of phosphorus lost in this way is entirely negligible. The amount of phosphorus in the fat was less than 0.06 per cent. in all cases, averaging about 0.02 per cent. of the weight of the fat, or calculated to the fresh skeleton was less than 0.003 per cent.

The phosphorus content reckoned upon the original substance gives about the same indication as does the ash. Those steers having the highest total moisture and fat content, or, in other words, those having the least solid matter are lowest in phosphorus. Calculated to the dry and fat-free basis, the phosphorus content also corresponds to that of the ash.

The composition of the ash, as indicated by the per cent. of phosphorus, varies in the different parts of the skeleton. The per cent. of phosphorus in the ash of the single cuts varies differently in the several steers and no conclusion will be attempted from the present data.

CONCLUSIONS.

(1) Young, growing steers continue to grow in height and build up skeleton even when losing in weight.

(2) The skeleton is unaffected by poor nutrition until practically all of the fat has been removed from the muscles and other organs.

(3) The principal effect of poor nutrition upon the skeleton is the removal of the fat or marrow and the replacement of this with water.

(4) The per cent. of organic matter other than fat is practically constant for the whole skeleton, under different conditions of nourishment.

(5) No evidence was obtained to warrant the conclusion that the mineral matter is resorbed or affected in amount due to lack of proper nourishment, although in steer 592 there is some indication that this may have taken place.

[1] Hart, McCullum and Fuller, *Am. Jour. Physiol.*, **23**, 246 (1909). Hart, McCullum and Humphrey, *Ibid.*, **23**, 86 (1909).

(6) The proportion of fat and moisture in the corresponding parts of the skeleton is fairly constant for normally fed steers. In steers which have suffered from insufficient nutrition for a long period the fat may be nearly all resorbed from the skeleton, and this resorption takes place from all parts of the skeleton.

(7) The proportion of organic and mineral matter in the skeleton varies with the age. This proportion varies in the different parts of the skeleton, according to the nature of the bone.

(8) The per cent. of phosphorus in the ash of the skeleton of steers is nearly constant. The per cent. of phosphorus in the ash of different parts of the skeleton of the same steer varies, but the average for the corresponding cuts of the five steers is fairly constant, showing a variation of not more than 0.7 per cent.

University of Missouri,
June, 1909.

EMIL CHR. HANSEN.

May 8, 1842–August 27, 1909.

Last year, on the 12th of November, an anniversary of no little importance was celebrated by the Carlsberg breweries in Copenhagen. On that day it was 25 years since the first pure culture yeast was introduced in the brewery of "Gamle Carlsberg." And to Emil Chr. Hansen justly went all the honors of the day.

Before Hansen made his epoch-making discoveries the brewing industry had been in the dark in regard to the causes of the very disturbing and often fatal troubles which occurred in the beer during fermentation and storage. Pasteur ascribed the diseases to the influence of bacteria and prescribed methods for the purification of the yeast, methods which in many cases not alone did not improve the conditions but even made them worse. Pasteur's methods were to cultivate the yeast in a sugar solution to which had been added tartaric acid or in beer-wort containing a small percentage of carbolic acid in order to destroy the bacteria. In many, and perhaps the most cases, however, the diseases of the beer were not due to bacteria but, as Hansen showed, to certain species of yeast, wild yeasts, and as the addition of tartaric acid and carbolic acid to the fermenting liquid did more damage to the good yeast than to the wild yeast, the result was the opposite of what was expected. The only solution which might prove satisfactory seemed to be the elimination of the wild yeast as well as the bacteria. But how? This Hansen accomplished by introducing his pure culture method. Hansen devised methods by which it was possible to distinguish between the different species of wild and culture yeast. Hansen, and not Robert Koch, was the first to introduce nutrient, transparent gelatine as a highly suitable medium in which to grow cultures. Hansen proved that by using pure cultures in the fermentation of the beer-wort, it was always possible to obtain the same result. If the starting yeast was kept pure and precautions were taken that no infection was introduced during the different stages of manufacture, the brewer would always be sure that he would obtain the same good and stable product. In connection with Kühle, the late director of "Gamle Carlsberg," he constructed a pure culture apparatus by means of which it was possible to work the pure cultures on a scale large enough for practical purposes.

From the time the pure culture yeast was first introduced in "Gamle Carlsberg" brewery, it has been a great success. With the generosity which always has characterized the Jacobsens (J. C. Jacobsen the founder of "Gamle Carlsberg," and his son, Carl Jacobsen), the discoveries of Hansen were given to the world, and every brewery in the old as well as in the new world has benefitted more from these than from any other discovery of modern times.

Not the breweries alone, but also the other branches of the fermentation industry: the distilleries, the compressed yeast factories, the wine factories have benefitted more or less from these same discoveries of Hansen. Also other industries have taken advantage of the pure cultures. Thus it was due to the introduction of the pure culture of lactic acid bacteria in the dairies that the Danish butter has reached the highest grade of perfection and won the reputation of being the best in the world.

Hansen limited his research work to the yeasts and to the bacteria which occur in the fermentation of beer, but these fungi he also pursued wherever and whenever he found them, not alone in the beer but also in the air, in the water, in the earth until they revealed their last life-secret to him. It is a fact that his results are final, at least, nobody has ever yet succeeded in disproving any of his printed statements.

Emil Chr. Hansen came from a poor family. His highly eccentric father was a painter by trade,

and the son learned the same trade before he came to Copenhagen. Here he first started to study with the intention of becoming an artist, but soon he changed and took up scientific studies. During his years of study he had to provide for his own living by teaching school and drawing pictures and writing stories for the magazines. In 1876 he won the University's gold medal for a treatise on certain fungi found in manure, and a few years later he took his degree as Phil. Dr. At this time he also participated in the translation of Darwin's books.

He was first connected with the "Ny Carlsberg" brewery, but as soon as the "Carlsberg Laboratory" (a research laboratory, founded by J. C. Jacobsen and maintained by "Gamle Carlsberg" brewery) was instituted, he was made director of one of its two departments, the physiological department, and here he worked until his death.

In the first years after his revolutionizing discoveries he met much opposition from both inside and outside Denmark, and the adversity seemed to weigh heavily on his shoulders, but even the faintest mumbling has stopped long ago and Emil Chr. Hansen has received the highest honors and recognition which it is possible to bestow on a man both from European governments and from the most important scientific bodies in the world.

His discoveries brought great fortunes to others. Hansen himself got nothing but his far from royal salary, but he was satisfied with a modest living and with small trips to the great art galleries of Europe; during his whole life he was a passionate lover of art.

At his death he did not leave much worldly goods, but he left a name for himself which will go down in history side by side by the names of Louis Pasteur and Robert Koch. NIELS C. ORTVED.

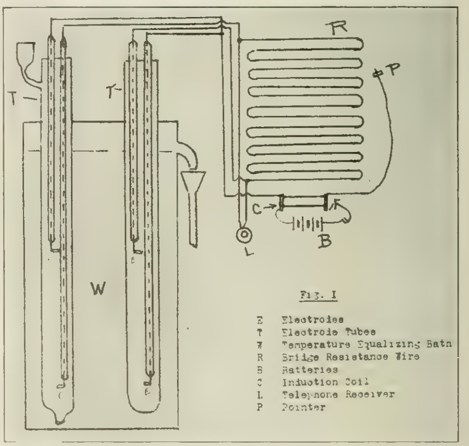
NOTES AND CORRESPONDENCE.

ELECTROTITRIMETER.

The "Electrotitrimeter" is an apparatus devised for testing the concentration of an electrolyte. It is based upon the fact that for many acids, alkalies and salt solutions the electrical conductivity varies with the concentration sufficiently to make the electrical test a method of accurate quantitative measurement. Temperature is such an important factor in conductivity work that a thermostat is usually used and the solution to be tested is brought to a given temperature before making the reading. According to Kohlrausch's method the results thus obtained are expressed in electrical units, the readings being made with a carefully calibrated rheostat. In the application of conductivity measurements for technical purposes, such apparatus is undesirable and by the use of the "Electrotitrimeter" it is unnecessary.

The difficulty of controlling the temperature has been overcome by the use of a compensating tube filled with a solution similar to the one to be tested, and when the apparatus is used for one purpose, such as for testing sulphuric acid of a certain strength, the tube is permanently sealed to prevent changes in concentration. This tube and the test tube are kept at the same temperature by immersing in a bath consisting of the solution which is being tested, or in another form of the apparatus the bath may be water.

The compensating tube and the test tube are each provided with two platinum electrodes and these are connected in such a way that each tube represents one arm of a Wheatstone bridge, and a high resistance calibrated wire represents



the other two arms. By means of a telephone and induction coil, a point is found on the bridge wire which shows the solutions in the two tubes to be in electrical equilibrium and any change in the concentration of the solution in the test tube causes this point to move. The wire is calibrated so as to read directly in percentage content of the solution to be tested.

The apparatus shown in Fig. 1 represents one form in which the electrolyte to be tested flows continuously through the test tube and then around both tubes forming the temperature equalizing bath.

In another form as shown in Fig. 2, the solution to be tested is poured into the test tube, the temperature equalizing bath being water in this case.

These tubes are each provided with glass stopcocks so that the solution in the compensating tube as well as in the test tube may be changed when different kinds of solutions are to be tested with the same apparatus.

When it is desired to control the strength of a product which flows continuously, a portion of the product is made to pass through the test tube, and with long connections

the reading part of the apparatus may be a considerable distance from the point to be tested. Any number of points may thus be connected with one reading apparatus. All that is necessary to make a determination at any point is to throw a switch making the connection, start the induction coil and with the telephone receiver at the ear, the pointer is moved along the bridge wire until the point of minimum sound is reached. The strength is then read off direct, the wire having been previously so calibrated when standardized.

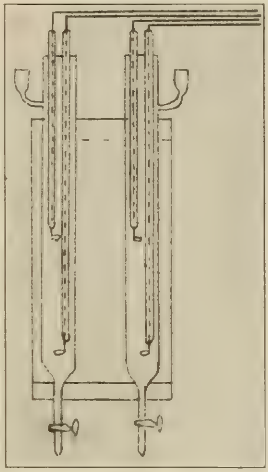


Fig. 2

With this simple apparatus, an unskilled laborer secures in a few seconds time results generally closer to the truth than those obtained by refined volumetric methods in the hands of a skilled analyst. This method is applicable for testing acids, water, solutions of various salts and alkalies. The sensitiveness in a few cases has been found to be approximately as follows:

		Per cent.	Per cent.	
Oleum		30 Free SO_3	0.01	Total SO_3
Sulphuric acid		100	0.01	H_2SO_4
" "		99	0.03	
" "		98	0.05	
" "		97	0.15	
Nitric acid		96–98	0.04	HNO_3
Salt solution	1–3 NaCl		0.02	NaCl
" "	3–5 NaCl		0.05	"
Sea water	(Atlantic)		0.0004	sp. gr.
Free HCl in bichloride of tin			0.04	HCl

This last is only slightly affected by a change of 1° Bé in the strength of the solution.

Patent rights have been secured in Canada and France, and applications are pending in other European countries and United States.

H. B. Bishop.

THE TECHNICAL DETERMINATION OF CAOUTCHOUC IN GUAYULE.

The rubber chemist is frequently required to determine the amount of caoutchouc in rubber-producing plants. As a rule the assay offers but little difficulty. Woody plants like guayule and pingué often give trouble Guayule is especially troublesome.

Where only small quantities are available an extractor, usually of the Soxhlet type, is used. A rapid economical way, suitable for technical work, is to make a double extraction; firstly, with acetone to dehydrate and to remove resin and, secondly, with some rubber solvent (carbon bisulfid, carbon tetrachlorid, chloroform, naphtha, etc.). The acetone extraction offers no difficulties excepting a possible carrying through of a little of the finely ground material. This can be remedied by efficient packing, and by returning the first portions of the percolate. Trouble begins after the addition of the rubber solvent when the thick rubber solution clogs the apparatus. The clogging can be remedied by the proper packing of the material in the barrel of the extractor. Use a large extractor. Pack firmly into the bottom a thick layer of clean, short-cut cotton waste. Take a metal rod of the required length, wrap it with several layers of flannel, securing the cloth with fine wire. Place one end of the prepared rod in the layer of waste, fill in the substance to be extracted—distributing it evenly around the core. Cover with a layer of waste. Place a small glass rod in the reservoir to prevent superheating and start the extractor slowly. The action of the syphon is a rough indicator of the richness of the sample and also of the progress of the extraction.

Operating the extractor by direct heat usually results in a broken flask. Single extractors are best heated with a water-bath, using either gas or electricity.

Extractors in battery formation give best results with steam.

Where a large number of determinations are to be made, and where it is desirable to control factory methods, small (1 pint or 1 quart size) ice-cream freezers in battery arrangement and operated by a small motor are desirable. One hundred grams are used as a charge. Benzol is used as the solvent; the resulting solution allowed to settle until clear and then alcohol added to complete precipitation. After settling of the precipitate decant the alcohol-benzol liquors, wash the precipitate, first, with a mixture of benzol and alcohol (precipitant in action), then with strong alcohol.

If quantity only is desired, the precipitated rubber is dried (vacuum preferred) on watch glasses or metal pans and weighed. Metal pans (copper) are preferred as they can be readily cleaned by burning. Scoring for quality requires that the precipitate be boiled with water to drive off solvents, then sheeted on the washing rolls and finally allowed to dry in a dark cool place. Clear, bright solutions give fine light rubber when dry. Cloudy, muddy solutions give black rubber.

Using finely cut material, duplicates give very uniform yields. Results are slightly low, owing to slight solubility of the caoutchouc in the benzol-alcohol mixture.

The most important part of the performance is the preparation of the sample. The guayule is a shrub, 10 to 30 inches high, and varying from 1 to 2 inches in diameter. The wood is very hard and bark thick. About 90 per cent. of the rubber is in the bark. With such conditions, to get a uniform sample for analytical purposes is a problem.

Usually, in a rubber factory the only available machine for pulverizing, is the common washing rolls with corrugated rolls.

The following experiments with this mode of grinding were made to determine the best stage of grinding. From the same shipment of shrub, five samples were prepared.

A. Coarsely ground. Many large pieces.

B. Ground medium fine. Obtained by re-grinding. Product more uniform than A.

C. Finely (?) ground. B reground until a sheet was obtained. Product not a uniform mass.

D. Medium fine. Sifted through a 1/4-inch mesh screen. Tendency towards separation between woody and barky portions.

E. Coarsely ground, ball-milled for two hours. Wood reduced to powder; bark reduced to small scales.

These samples were extracted in a Soxhlet with acetone, and then by carbon bisulfid, the extracts dried at 100° C. and weighed. The table shows the results.

	Acetone extract, resin.				Carbon bisulfid extract, rubber.			
Preparation.	(1)	(2)	Av.	Var.	(1)	(2)	Av.	Var.
A. Coarsely ground..	9.91	9.84	9.88	0.07	9.77	10.95	10.41	1.18
B. Medium fine......	9.16	8.84	9.00	0.32	9.34	9.44	9.39	0.10
C. Finely (?) ground	9.90	9.74	9.82	0.16	7.33	8.71	8.02	1.38
D. Medium ground, sifted.	9.97	10.77	10.42	0.88	8.68	9.88	9.28	1.20
E. Coarsely ground, ball-milled.....	9.63	9.54	9.74	0.21	7.88	9.29	8.58	1.41

An examination of these results reveals:

1st. That none of the methods of preparation are perfect.

2nd. That the regrinding system, (B) when carefully carried out, gives best results.

3rd. That the rubber content seems inversely proportional to the degree of fineness.

This is probably due to a more even distribution of the rubbery (barky) portion throughout the entire mass. In coarsely ground sample the barky portions, due to gravity, are usually on top and an undue proportion gets into the assay charge.

4th. That the tendency of the bark particles on account of their rubber content, as determined by the initial grinding or crushing, is to amalgamate in opposition to heavy milling or ball-milling and sifting combined, and that a cutting system is demanded.

CHAS. P. FOX.

RECENT INVESTIGATIONS OF FATS AND OILS.

In the first number of THIS JOURNAL[1] I contributed a brief account of some work, carried out by Professor Paal, of Erlangen, on the catalytic reduction of fats and oils. The number of letters on the subject which I have received suggests that a further report on some subsequent investigations may prove to be of interest. The method of experiment consisted in emulsifying the fat or oil with an aqueous solution of gum arabic adding a little colloidal palladium, also dissolved in water. The remainder of the vessel was filled with hydrogen and it was shaken at the ordinary temperature, until the volume of gas remained constant. The relative quantities of fat and palladium which were employed differed within rather wide limits, in one case, which may be taken as fairly typical, the ratio of metal: fat was 1:500. In their most recent communication Paal and Roth[2] describe experiments with castor, croton, olive, sesame, cottonseed and linseed oils and with butter fat, lard and oleomargarin (from beef suet). In some cases complete reduction was only attained by a second or even a third treatment with hydrogen and colloidal palladium. The reduced fats and oils are in general, colorless solids, which melt at definite temperatures, ranging from about 45–70°. The compounds from croton and castor oils fail to exhibit any physiological activity. As a rule these reduction products are without taste or odor, but that from butter has a pleasant nutty flavor and a faint odor of the mother substance is noticeable in the castor oil derivative.

[1] Vol. **1**, 47.

[2] *Ber.*, **42**, 1541.

One of the most interesting points brought out in the course of the work is the lack of connection between the quantity of iodine and that of hydrogen with which a given fat or oil can combine.

It has been generally supposed that the additive power of a fat for hydrogen, iodine, or iodine chloride was dependent on the double (ethylene) linkages which were present. This, however, is by no means the only factor to be considered and it is necessary to recognize clearly that the addition of hydrogen and of iodine are quite independent reactions which proceed on parallel, but by no means on identical lines.

All the fats and oils mentioned above absorbed more hydrogen than the quantity calculated from their iodine numbers and the excess was quite considerable, amounting to over 25% in the case of linseed oil, to more than 50% in that of lard and, with the cottonseed oil, to almost 100%.

The reduced fats, although containing this "excess" of hydrogen are, in some cases, still capable of combining with iodine. The product from sesame oil and also that from oleomargarin, for example, have iodine numbers of 2 and 1.2, respectively.

This compound from sesame oil (iodine number 2) exhibits Baudouin's test only very feebly. After remaining during eight months the fat gives the Baudouin color quite strongly, although its iodine number is not changed. It is evident that the particular substance which is present in sesame oil, and on which the Baudouin test depends, is reduced by the hydrogen but is regenerated, to some extent at least, on exposure to air. The reduced fat from cottonseed oil fails to show either the Becchi or the Halphen tests. In general, these reduced fats are quite stable in air and exhibit no sign of rancidity.

In another paper,[1] Paal and Hartmann show that a minute quantity of colloidal palladium solution is able to bring about the combination of ethylene and hydrogen. The liquid was shaken in a closed vessel, containing the two gases, at the ordinary temperature. The union of the gases was quantitative. This result is of considerable interest in connection with the reactions involved in the reduction of fats and oils.

The problem of the fats has been attacked in another manner by Quensell,[2] who has synthesized a number of the glyceryl esters of stearolic acid and also those of behenolic acid. From some of these esters he has prepared a number of halogen addition compounds. The first molecule of halogen is added by the acid radicle without difficulty, but combination with a second molecule takes place only slowly and in presence of light. In these respects the glyceryl esters resemble the free acids. In dealing with the diacylated glycerols, Quensell unfortunately fails to state which of the isomers, $HOCH_2CH(OX)CH_2OX$ or $XOCH_2CH(OH)CH_2OX$ ($X = C_{18}H_{31}O$ or $C_{22}H_{39}O$), he employed in his experiments with halogens, so that the value of his results is lessened.

J. BISHOP TINGLE.

MCMASTER UNIVERSITY, TORONTO, CANADA.
Aug., 1909.

CORRECTED QUALITY FIGURES.

In the July number of THIS JOURNAL, the writer criticizes Turner's rule for getting quality figures as being

[1] *Ber.*, **42**, 2239.

[2] *Ibid.*, **42**, 2440.

wrong in principle and giving, therefore, misleading results, and proposed a rule of his own which, however, upon further study, is seen to be also wrong (although to a lesser degree) *when any factor happens to be abnormally low*, and he therefore begs to substitute the following:

Find what per cent. the elastic limit of the steel under consideration is of the very best elastic limit that could be possible (always thereafter adhering to this best elastic limit as a standard, and so also of the other factors), what per cent. the shock or alternation figure is of the best, what per cent. the hardness is of the best. Add them together and divide by three.

According to this rule the quality figures given in the above-mentioned paper come as follows: Standard, elastic limit, 200. Shock, 20. Hardness, 600.

QUENCHED VANADIUM NICKEL STEELS.

Composition.			Quality figure.
C 0.20	Ni 6	Va 50	0.5570
C 0.20	Ni 6	Va 70	0.4433

QUENCHED CHROMIUM, ETC. NICKEL STEELS.

C 0.20	Ni 6	Cr 0.50	0.5653
C 0.20	Ni 5	Cr 1.0	0.6583
C 0.20	Ni 6	Cr 1.0	0.5422
C 0.20	Ni 5	Cr 3.0	0.5055
C 0.20	Ni 6	W 2.0	0.6050
C 0.20	Ni 6	Wo 30	0.5900
C 0.20	Ni 5	Wo 30	0.5939
C 0.20	Ni 6	Mo 1.0	0.5072
C 0.20	Ni 6	Mo 0.50	0.6030
C 0.20	Ni 6	Mo 2.0	0.5317
C 0.20	Ni 6	Si 0.50	0.5839
C 0.20	Ni 6	Si 0.80	0.6133

QUENCHED VANADIUM NICKEL STEELS.

C 0.20	Ni 2	Va 30.0	0.5600
C 0.20	Ni 2	Va 1.0	0.4636

QUENCHED SILICON NICKEL STEELS.

C 0.20	Ni 2	Si 1.5	0.4603
C 0.20	Ni 2	Si 1.0	0.5252
C 0.20	Ni 2	Si 0.50	0.6131

NORMAL VANADIUM NICKEL STEELS.

C 0.20	Ni 6	Va 30.0	0.3693
C 0.20	Ni 6	Va 50.0	0.3609
C 0.20	Ni 6	Va 70.0	0.3897

NORMAL CHROMIUM NICKEL STEELS.

C 0.20	Ni 5	Cr 1.0	0.5628
C 0.20	Ni 6	Cr 1.0	0.4639
C 0.20	Ni 6	Cr 2.0	0.5467

NORMAL TUNGSTEN NICKEL STEELS.

C 0.20	Ni 6	W 1.0	0.4517
C 0.20	Ni 6	W 2.0	0.4100
C 0.20	Ni 6	W 6.0	0.4319

NORMAL MOLYBDENUM NICKEL STEELS.

C 0.20	Ni 6	Mo 0.50	0.5203
C 0.20	Ni 6	Mo 1.0	0.5064
C 0.20	Ni 6	Mo 2.0	0.4561
C 0.20	Ni 6	Mo 5.0	0.4311

NORMAL SILICON NICKEL STEELS.

C 0.20	Ni 6	Si 0.50	0.5094
C 0.20	Ni 6	Si 0.80	0.3144
C 0.20	Ni 6	Si 1.0	0.2822
C 0.20	Ni 5	Si 2.0	0.2722
C 0.20	Ni 6	Si 2.0	0.3511

Mr. Turner's Tests.—Standard, 200,000 elastic limit. 2000 alternations. Not comparable with preceding.

Vanadium Chrome Steels.—No. 15, 0.5568; No. 17, 0.5203; No. 23, 0.6083; No. 24, 0.5333; No. 27, 0.6170.

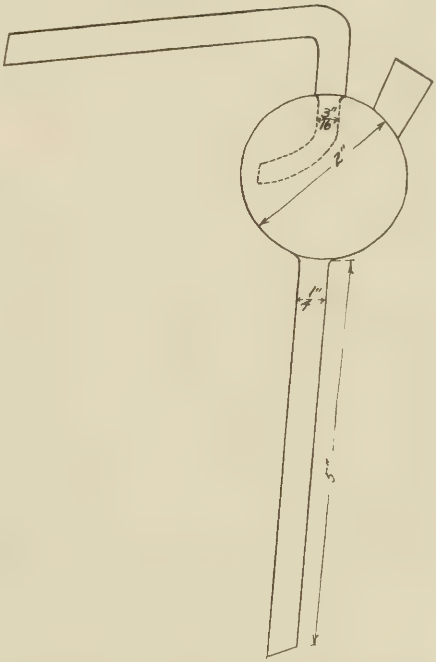
Nickel Chrome Steels.—No. 9, 0.3858; No. 21, 0.3907; No. 28, 0.4810.

GEORGE AUCHY.

A MODIFIED KJELDAHL CONNECTING BULB.

A modification of the Kjeldahl connecting bulb, which is not only useful but also tends toward greater accuracy in ammonia determination, is represented in the drawing. This was designed primarily for ammonia determinations in water but will, no doubt, find favor in other ammonia determinations as well.

The drawing speaks for itself, so there is little need for an explanation of the modified apparatus. Chemists making an ammonia determination in water with a Kjeldahl flask connected to a condenser by a Kjeldahl bulb pursue



a method which is capable of greater experimental error than it should be. In an effort to lessen this experimental error, the above modification was made. With the old style of bulb it was necessary, after freeing the apparatus of ammonia, to remove the rubber stopper containing the connecting bulb and pour it through the neck of the flask, the sample of water to be analyzed. The stopper had to be removed again when introducing the alkaline permanganate for the determination of the albuminoid ammonia. This makes possible the introduction of ammonia into the apparatus which has previously been carefully freed of ammonia. With the modified connecting bulb, the opening in the bulb

is much smaller and is far removed from the body of the flask, and the danger of contamination with ammonia when the stopper is out of this opening while introducing the water sample and the alkaline permanganate solution is reduced to a minimum.

The writer has used this form of the Kjeldahl connecting bulb for more than a year and has found it very satisfactory. They were made for the writer by E. H. Sargent & Co., of Chicago.

C. A. JENNINGS.
CHIEF CHEMIST AND SUPERINTENDENT OF FILTRATION, UNION STOCK YARD AND TRANSIT CO., CHICAGO.

A SIMPLIFIED COMBUSTION CRUCIBLE.

In 1899 the writer published a paper[1] describing an ordinary platinum crucible which, for combustion purposes, could be closed by means of a water-cooled brass stopper fitted with a rubber band and provided with inlet and outlet tubes. In 1901 he described a special water-jacketed crucible[2] to be used in connection with the water-cooled stopper. This latter form has come into rather extensive use. A disadvantage, however, is its rather high cost, the 60 cc. size weighing about 92 grams; it is also rather difficult to manufacture and repair.

In the latest form of the apparatus[3] the crucible is a simple one, without the water jacket. It is 60 cc. capacity, rather deep in form, and weighs only 50 grams. When provided with an ordinary cover, to be used when making fusions, the weight is 57 grams. The crucible is accurately fitted with a rigid knurled ring around its upper part, easily removable. The water-cooled German silver stopper, instead of having a rubber band to secure a tight joint, is ground into the crucible. This joint may easily be kept tight by an occasional grinding in, using for this purpose a little glass, finely ground in the agate mortar with oil.

A very good way to secure absolute tightness and, at the same time, a certain lubrication, is to melt the rubber at the extreme end of a "policeman" in the flame and apply the minutest amount possible at intervals around the upper edge of the crucible. Now insert the stopper tightly with a turning motion. One milligram of rubber is enough for the purpose and the water circulation prevents this from being affected by the heat.

The advantages of this form of apparatus over the older form are:

1. The 60 cc. crucible weighs about 40 grams less and, on account of its simple form, it is less expensive to make.

2. When provided with an ordinary platinum cover it is a fusion crucible, on removal of the ring. Its deep form is desirable for fusions. This ready adaptability for both combustions and fusions is an advantage in any laboratory, especially the small one in which platinum is limited.

3. By doing away with the rubber band there is no risk of losing a determination in case the water supply fails temporarily.

4. The knurled ring protects the mouth of the crucible from injury and stretching, supports the crucible at the proper height in the asbestos board, and helps to secure a tight joint.

5. It is more convenient than the older form because it may be removed easily from its support for charging; this is especially advantageous in direct combustions of steel.

6. Smaller cost of repairs and renewals.

The writer, nearly ten years ago, tried nickel in place of platinum, but found it more expensive in the long run and otherwise less desirable. It is estimated that one carbon

FIG. I.

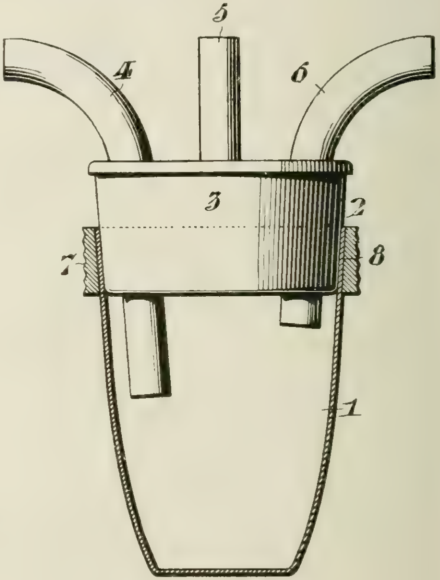
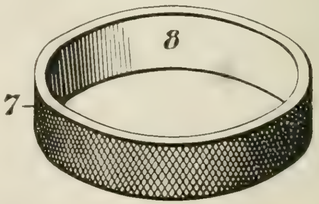


FIG. II.



combustion in a 60 cc. platinum crucible costs about 1/3 of one cent for platinum, counting interest on the investment, repairs and final scrapping. The short life of a nickel crucible makes each combustion cost about 3 cents in nickel, with risks of faulty results toward the end of the life of the crucible.

The train for carbon determination is as follows: 1. The oxygen tank. 2. KOH bulbs. 3. A small guard bulb. 4. The

[1] *Jour. Am. Chem. Soc.*, **21**, 1899. "Carbon Combustions in a Platinum Crucible."

[2] *Ibid.*, **23**.—"A Spiral Crucible for Carbon Combustions."

[3] Patented 1909.

crucible. 5. The burner. 6. A water-jacketed brass CuO tube. 7. The zinc tube according to Johnson. 8. Calcium chloride tube. 9. Soda-lime U-tube or other absorbent. 10. A small guard tube of $CeCl_2$. 11. An empty bottle provided with inlet and outlet tubes, the latter dipping under the surface of water contained in a small beaker for the purpose of noting the rate of flow of oxygen in direct combustions. The CuO tube is used only when making carbon determinations by the solution method and for organic combustions; for direct combustion of steel it is not needed. As a source of heat, a good Bunsen burner with a hot "roaring" flame is sufficient for most purposes. In many combustions, however, the upright blast lamp is necessary. For absorbent, a soda lime U-tube weighing, when filled, anywhere from 50 to 100 grams, is used. The soda lime should be about 20-mesh in size and free from powder.

Drillings of steel for direct combustion should be thin and should be between 20- and 60-mesh in size. As a base for the drillings a great many substances have been proposed and the writer has tried most of them, among them sesquioxide of iron both in the form of rich hemetite ore and chemically pure sesquioxide. With the latter good results may be obtained, but it is rather hard to get it reliably free from "blank." Very satisfactory results may be obtained by using sea sand previously washed and well ignited. The grains are rounded; it holds the fused oxide well and leaves the crucible clean.

In charging the crucible, put in not less than 1/4 inch deep of the sand, hollow out a little depression and pour the drillings into the middle of it through a funnel with wide and short stem. Cover the drillings with a mixture of finely divided ignited asbestos and powdered CuO. One-half the factor weight (1.3635 gram) is the usual weight of steel used. Combustion should be active in from 1 to 3 minutes and should be complete in 20 minutes or less.

Carbon in pig-iron may be determined by direct combustion on the sand, without admixture, but it is best to use the blast lamp. When red lead is used it is, of course, necessary to use a porcelain crucible, with sand, inside the platinum crucible.

In determining carbon in ferro-chrome, very good results were attained by burning on the sand a very intimate mixture (mixed on glazed paper with spatula) of 0.6818 gram of the finely ground ferro-chrome with four times its weight of powdered CuO.

A little experience and observation will soon indicate the best way to make direct combustions in the various steels and alloys, but it is always best to avoid coarse or thick drillings and brittle alloys should be finely pulverized. It is always well, when in any doubt as to the completeness of the combustion, to examine the fused mass for metallic particles by grinding in a mortar.

A few results follow:

	By solution and combustion.	By direct combustion.
Straight steels	0.137	0.137
	0.240	0.239
	0.424	0.420
	0.600	0.603
	0.829	0.823
	1.036	1.035
	0.627	0.628
	0.452	0.456
Pig iron	3.62	3.64
Ferro chrome	7.09	7.10	7.12
Alloy steel—W. Cr. V.		0.450	0.444
" " Ni. Cr. V.		0.920	0.916
" " Ni. Cr. V.		0.660	0.666
" " W. Cr. V.		0.542	0.550
" " Ni. Cr		0.194	0.196
" " Cr. V.		0.998	1.000

PORTER W. SHIMER.

EASTON, PA

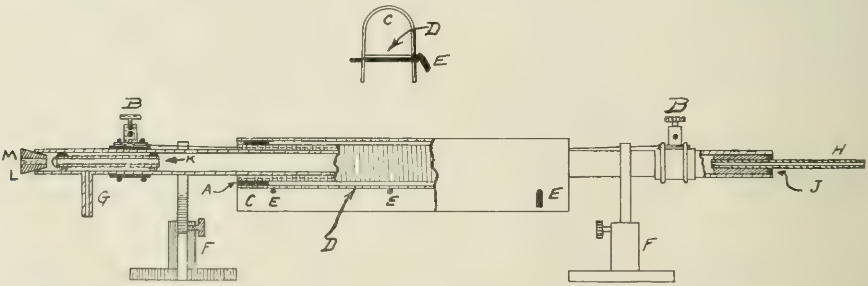
NOTE ON A RAPID COOLING ELECTRICALLY HEATED COMBUSTION TUBE.

The object aimed at in designing the furnace described below was to devise a combustion tube which would combine the advantage of rapid and equal heating of an electrically heated combustion tube with the rapid cooling of a gas-heated combustion furnace. Most electrically heated furnaces are so carefully insulated against loss of heat by radiation that when the heating current is cut off the cooling of the furnace is very slow. Fused silica combustion tubes have been used so that a cold combustion boat could be pushed into a hot tube without danger of cracking the latter. Experience in this laboratory has gone to show that if the combustion boat, containing the sample, particularly iron or steel, can be put into a cold or nearly cold furnace, and the temperature raised to about 900°, that complete combustion of the carbon can be readily effected without danger of the residual oxides spattering, thus endangering the tube. Porcelain combustion boats, provided with a thin sheet platinum lining, are usually preferred by the author.

The combustion furnace, which has given very satisfactory results in this laboratory, is made from a porcelain combustion tube, 78 cm. long, 24 mm. inside, and 30 mm. outside diameter, provided with a side arm about 5 cm. from one end. A tube of fused silica might easily be substituted for the porcelain tube, but the silica tubes are not made with side arms, and are usually not made true enough to be easily stopped gas-tight with a rubber stopper. With the system of winding used in the furnace to be described, there is not much danger of cracking a porcelain tube by too rapid heating.

For electric heating, the tube is wound with a "Nichrome" ribbon, 4.7 mm. (3/16 inch) wide and 0.1 mm. (0.004 inch) in thickness. The general construction of the furnace is shown in the accompanying sketch. The wound portion in the central part of the tube is about 38 cm. in length. Before winding with the nichrome ribbon, this portion of the tube was wrapped with two thicknesses of thin, pure asbestos paper, laid on wet with water only. The nichrome ribbon was bent at right angles and at the bent portion was wired to the asbestos with a piece of nichrome or nickel wire. The tube was then wound spirally, the space between adjoining spirals being about two mm. When this first winding was complete, the end was again wired, the ribbon bent at right angles, and carried along the top of the tube for connection with the binding posts, B. When the inner winding had been put on, this was wrapped with four thicknesses of thin pure asbestos paper, extending about one cm. beyond the beginning of the spiral wind. The four outer layers of asbestos were put on wet with water only,

and outside of this a second winding of nichrome ribbon was wound. This outer layer of nichrome ribbon is wound with the edges close together, thus forming a practically continuous thin metal jacket, insulated from the inner nichrome winding, but serving to prevent the asbestos from crumbling and falling off after heating. At each end of the nichrome jacket, which was prevented from unwinding by wiring with nichrome or nickel wire, a collar, A, about 30 mm. wide and 8 mm. thick, was made by winding that portion with a strip of thin asbestos wet with a dilute solution of sodium silicate. The binding posts, B, were first soldered to a strip of copper, the width of the binding post, and about 30 mm. long. The second strip of copper, of the same size, could be fastened to the under side of the binding post by means of a screw. Connection with the nichrome ribbon is made by inserting it between these two copper strips before tightening the screw. Each binding post was attached to the porcelain tube by first wrapping the latter with a strip of asbestos, wet with dilute sodium silicate, thus making a collar about 40 mm. wide and 3 or 4 mm. thick. The binding post was then placed on this collar and firmly fastened by means of a couple of wires. After the nichrome windings were complete, and connection made to the binding posts, the tube was thoroughly dried to the porcelain tube by packing the space, J, with a stiff mixture of talc and diluted sodium silicate. When this latter mixture has been thoroughly dried in the drying oven, the tube was evacuated and the joint at J made permanently gas-tight by applying hot rubber cement. When in use, the portion of the porcelain tube from the nichrome jacket to the outlet end is filled with pieces of porous ware, and the heated portion of the tube, for a distance of about 10 cm., is filled with similar pieces which have been platinized by first saturating with a dilute solution of platinic chloride, and subsequently drying and igniting at a bright red heat. After the boat containing the sample has been pushed into the furnace, a porcelain plug, K, about 12 cm. long is put in in order to prevent radiated heat from affecting the rubber stopper, L. The plug, K, consists of a piece of porcelain tubing 12 mm. inside diameter, provided with a nickel wire loop at one end and silicated asbestos collars at both ends, these collars increasing the diameter almost to that of the inside diameter of the combustion tube. The rubber stopper, L, used for closing the open end of the combustion tube, contains a piece of clear glass rod, M, cut the length of the stopper and polished at both ends. Through this glass, and the hollow plug K, the color of the interior of the combustion tube may be readily observed.



in a drying oven, in order to harden the asbestos collars at the ends of the nichrome jacket, and under the binding posts. In order to prevent loss of heat, the removable mantle, C, was made, by thoroughly wetting with sodium silicate three or four thicknesses of heavy sheet asbestos, and shaping it over a piece of tubing a little larger in diameter than the collars, A. Asbestos soaked in a solution of sodium silicate, diluted with twice its volume of water, after drying, became quite hard and strong, and has been found very useful in this laboratory for a good many years. The mantle, C, is provided with a loosely fitting bottom, D, made from a strip of heavy asbestos board hardened with sodium silicate. The mantle bottom, D, when the furnace is in use, rests upon three heavy wire pins, E, passing through the mantle. If these pins are pulled out, the bottom and mantle can be easily removed, thus permitting the furnace to cool quickly; at the same time the asbestos and nichrome jacket are sufficiently thick to prevent the tube from cracking. When in use, the combustion tube is supported by means of two adjustable supports, F.

Oxygen for combustion is admitted through the side arm, G, and the products of combustion pass out through the thick-walled glass tube, H. This glass tube is cemented

The heating current is controlled and measured by means of a rheostat and ammeter, kept in the circuit during the working. When testing the rate of heating and cooling, a standardized platinum rhodium thermocouple was inserted into the furnace in place of the combustion boat. With the heating current maintained at 8.3 amperes the thermocouple showed a temperature of 500° in five minutes and thirty seconds, 600° in seven minutes and fifteen seconds, 700° in nine minutes and fifteen seconds, 800° in twelve minutes, 900° in fifteen minutes and fifteen seconds, 950° in nineteen minutes and thirty seconds. Nine hundred degrees is hot enough for direct carbon combustions in iron and steel, and 7.9 amperes was the current required to maintain the furnace at this temperature.

Starting with a temperature of 934°, the rate of cooling is shown in the following table, which gives the temperature at intervals of two minutes:

Time in minutes.	Temperature in degrees centigrade.
0	935.0
2	800.0
4	650.0
6	529.0
8	435.0

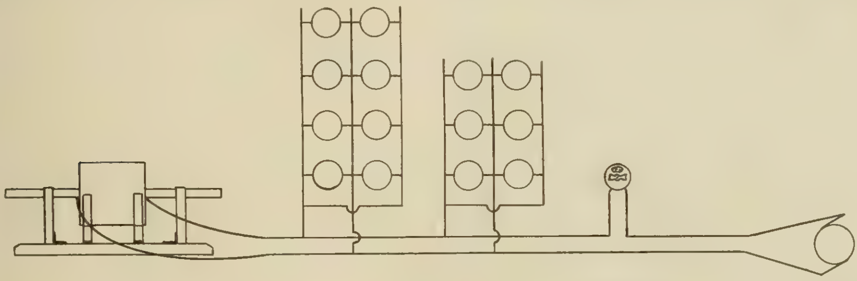
Time in minutes.	Temperature in degrees centigrade.
10	368.0
12	314.0
14	271.0
16	238.0
18	206.0
20	180.0
22	158.0
24	140.0
26	125.0
28	112.0
30	100.0

EDWARD DEMILLE CAMPBELL,
EDGAR NATHANIEL GOTT.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN;
ANN ARBOR.

HOME-MADE ELECTRIC FURNACE.

In view of the fact that the writer has received a great many inquiries as to the method of making the electric furnace referred to in the article entitled "Economy in the Use of Oxygen, Etc.," [1] he believes that a note describing the same may be of interest to others.



The furnace is strictly "home-made" and gives excellent service. As before brefly explained, it is a porcelain tube wound with a platinum resistance and jacketed with pipe coverings. A porcelain tube is to be preferred to one of quartz on account of the repeated annealing it has to undergo in cooling off every night. The condition of the former is improved by such treatment, but the latter assumes a crystalline structure and becomes very brittle. The tube should be about two feet long and one inch in diameter. The resistance is a strip of platinum foil, 8 feet long, 4 mm. wide, and about 10 mm. thick, with the last four inches of each end left about 10 mm. wide in order to have metal enough to make a good cool connection with the circuit.

To make up the furnace, moisten a piece of sheet asbestos 16″ long by 1/16″ thick, and wide enough to encircle the tube, and wrap it once around the tube, having first covered the latter with a little water glass solution. Make a couple of clamps of sheet nickel. These are bands about 1/2″ wide and 1/32″ thick clamped together with small bolts and nuts and are intended to hold the two ends of the foil. Put them on about six inches from each end of the tube and clamp one end of the foil under one of them, letting it project far enough for a connection and wind the strip of platinum tightly around the tube, leaving about 1/4″ or more between turns and fasten with the clamp at the other end, allowing it to project in a similar manner for connection with the current. The length of the tube wound with resistance should be about 9″ and not more than 10″. Cover this with a plaster about 1/8″ to 1/4″ thick made of broken up pipe covering mixed with water and enough fire clay to act as a binder, putting it on in much the same way as frosting is put on a cake, thus enclosing the resistance in an infusible casing which proves very efficient in preventing a short circuit. Next cut off a piece of magnesia pipe covering (1 3/4″ inside diam.) 9″ long and put it around the tube, replacing the cloth cover with asbestos and fasten it on with a few turns of iron wire. Prepare a stand similar to that in the illustration (scale: 1/2″ = 1′) in THIS JOURNAL and place on the iron brackets of the stand two pieces of pipe covering, one inside the other, the outside one having an inside diameter of 7″, and the inside one an outside diameter of 7″.

Slip the tube into its position and strap it down with pieces of leather thong to the two uprights—these should be of such a height above the brackets as to support the tube independently of the outside jacket—then plaster up each end of the jacket with a paste of pulverized pipe covering or of asbestos cement and the furnace is ready for use.

Sometimes the heat fuses the inside of the tube a little, but when this is the case, magnesium oxide spread out on the inner surface will soon prevent any further trouble. It is necessary to use a nickel rod or wire to push the boat into the tube, as an iron rod becomes magnetized and will pull the drillings from the boat on being withdrawn.

We are at present using this furnace on a 220 volt direct current circuit in series with a lamp back of twelve to fourteen one ampere (100 c. p.) lamps. This gives a current of about 12 amperes with a drop across the furnace of 30 to 35 volts and a temperature of 1100° to 1200° C. This, of course, can be regulated to almost any degree by changing the number of lamps. It is possible to attain a temperature of 1500° C., but it is not advisable to run it as high as that, both on account of the liability of a burn-out and the loss of platinum by volatilization. In case a burn-out occurs it is a simple matter to weld the foil electrically, thus making quick repairs possible. In fact it is possible to entirely dismantle and rebuild this furnace in less than an hour. The cost of the furnace need not exceed $30, and it

[1] THIS JOURNAL, 1, 375.

may be made for much less and operated with much less power if a thinner foil is used as a resistance. The dimensions given, however, are preferable for furnaces in continuous operation. The ideal method of using such a furnace is in conjunction with a motor-generator set, but the following sketch will show the method of wiring above described. WM. HERBERT KEEN.

LABORATORY OF THE FILTH
STERLING STEEL CO.,
WASHINGTON, D. C.

BOOK REVIEWS AND NOTICES.

The Lead and Zinc Pigments. By CLIFFORD DYER HOLLEY, M.S., PH.D., Chief Chemist, Acme White Lead and Color Works. 12mo. xv + 340 pp., 85 figures. Cloth, $3.00 net. New York: John Wiley & Sons.

The thirty-one chapters of this book contain much that is of interest and value. Much of the matter is of a historical and descriptive nature. The analytical methods are in the main adequate. Among the defects of the work are selection of illustrations of superficial rather than intrinsic merit (notably the frontispiece), and the addition of an appendix containing tables which are already in the possession of all chemists in books of more convenient form.

The Scientific and Industrial Bulletin of Roure, Bertrand Fils, of Grasse, for April, 1909 (Series 2, No. 9), while appearing rather late contains much matter of interest in connection with essential oils. Among other articles are these: "The Resin Industry of the Landes;" "Contribution to the Study of Perfume-Yielding Plants;" "The Suppression of Fraud So Far as Essential Oils Are Concerned;" "Review of Recent Work on the Perfumes and Essential Oils." 8vo. pp. 160.

The Mineral Content of Illinois Waters. Bulletin No. 4 Illinois State Water Survey. Prepared in Coöperation with the State Geological Survey. By EDWARD BARTOW, J. A. UDDEN, S. W. PARR, and GEORGE T. PALMER, Urbana, 1909.

This volume contains an introduction by Edward Bartow; Geological Classification of the Waters of Illinois, by J. A. Udden, Classification of Mineral Waters, According to Physical and Chemical Properties, by Edward Bartow; Methods and Interpretations, by Edward Bartow; Boiler Waters, by S. W. Parr; Mineral Springs of Illinois, by George T. Palmer, M.D.

NEW BOOKS.

This list was prepared by Mr. Paul Escher, 1319 Pearl Street, Alameda, California.

Agricultural Chemistry.

Moisture Content and Shrinkage in Grain. By J. W. T. DUVEL. pp. 13. (Circular 32, Bureau of Plant Industry.)

Agriculture for Southern Schools. By JOHN FREDERICK DUGGAR. Louisiana edition. MacMillan Co., New York. Ill., 12. $.60x. Cloth, xi. 340 pp. xlii pp., index.

Fertilizers.

Artificial Manures: Their Chemical Selection and Scientific Application to Agriculture. By M. GEORGE VILLE, translated and edited by SIR WILLIAM CROOKES. New edition revised by SIR WILLIAM CROOKES, D.SC., F.R.S., and JOHN PERCIVAL, M.A. 6 plates. 8vo. pp. xl, 348. Longmans, Green & Co., London and New York. Price, $3.00 net.

Chemical Conversion Tables. For use in the analysis of fertilizers, fertilizing materials, iron and its products, etc. By H. B. BATTLE, PH.D., and W. J. GASCOYNE, PH.D. Pocket size, indented reference index. Williams & Wilkins Pub. Co., Baltimore, Md. Price, $2.50.

Mining and Metallurgy.

Antimony. By WANG CHUNG YU. J. B. Lippincott Co., Philadelphia. 1909. Price, $4.00.

The Nature of Ore Deposits. Translated and revised by W. H. WEED. R. BECK. 1909. Hill Publishing Co., New York. $6.00.

Fuel.

On the Rate of Formation of Carbon Monoxide in Gas Producers. By J. K. CLEMENT, University of Illinois, Urbana. 1909.

Das Erdöl, Seine Physik, Chemie, Geologie, Technologie, Etc. By C. ENGLER and H. HOFER. 5 bände. Band 2. Geologie, Gewinnung und Transport. Mk. 46, geb. 50.

Paints.

Lead and Zinc Pigments. By C. D. HOLLEY. John Wiley & Sons. New York. Price, $3.00.

Industrial Chemistry.

Chemistry for Engineers and Manufacturers. By B. BLOUNT and A. G. BLOXAM. Vol. II. The Chemistry of Manufacturing Processes. 8vo., cloth. Ill., 514 pp. J. B Lippincott Co., Philadelphia. Price, $4.00.

Cane Sugar and Its Manufacture. By H. C. PRINSEN GEERLIGS. Large 8vo., pp. 350. 12s. Norman Rodger, Altrincham, Manchester.

Tables and Diagrams of the Thermal Properties of Saturated and Supersaturated Steam. By LIONEL S. MARKS, M.M.E., and HARVEY N. DAVIS., PH.D. Large 8vo., pp. 106. Longmans, Green & Co., London and New York. $1.00 net; by mail $1.10.

Die Fabrikation der Lacke, Firnisse und des Siegellacks. By ERICH DETTMERS. (116 Band. Bibliothek der gesamten Technik.) 8 dbb. Mk. 2.60. M. Janecke, Hannover.

Chemisches Auskunftsbuch für Fabrikanten, Gewerbetreibende und Landwirke. By HUGO KRAUSE. A. Hartleben, Leipzig und Wien. Mk. 4.80.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS.

The thirteenth annual convention of the Association of State and National Food and Dairy Departments was held at the Brown Palace Hotel, Denver, Colo., August 24–27, 1909. On the opening day, August 24, addresses of wel-

come were made by the Governor of Colorado, the Mayor of Denver, and the Secretary of the State Board of Health, followed by a response by Food Commissioner A. C. Bird, of Michigan. President J. Q. Emery, of Wisconsin, then delivered his address in which he noted the progress made by the association during the year. He discussed at length the question of benzoate of soda and criticized the findings of the Referee Board appointed to investigate its effect on health when present in food products. By general request Hon. James Wilson, Secretary of Agriculture, then addressed the Association, defending the Referee Board and calling for its fair treatment at the hands of the Association.

During the afternoon session five minute speeches were made in the most salient features in the food, dairy and drug control work of the respective states, by the various commissioners, executive officers and visiting chemists representing the states that follow: California, Colorado, District of Columbia, Georgia, Illinois, Idaho, Indiana, Iowa, Kansas, Kentucky, Louisiana, Maine, Maryland, Massachusetts, Michigan, Minnesota, Missouri, Nebraska, New Jersey, New York, North Carolina, North Dakota, Ohio, Oklahoma, Oregon, Pennsylvania, South Dakota, Tennessee, Texas, Utah, Wyoming and Wisconsin. A food chemist's conference was listed for Tuesday afternoon, but was not held.

On Wednesday the delegates and guests enjoyed a complimentary, all-day mountain trip through Clear Creek Canyon over the Georgetown Loop and to the summit of Mt. McClellan, over 14,000 feet above the sea.

On Wednesday evening a meeting was held at which Commissioner E. F. Ladd, of North Dakota, addressed the Association on a Model State Food Law, and Commissioner H. E. Barnard, of Indiana, spoke on Sanitary Inspection of Food Products and Distribution.

Thursday's program opened with a discussion of the report of the Referee Board on sodium benzoate, beginning with short addresses by Doctors Ira Remsen, R. H. Chittenden, John H. Long and C. H. Herter, members of the Board. This was followed by a brief report of a committee of State Food Chemists, appointed by the executive committee to review the experiments and conclusions of the Referee Board, the members of that committee being Messrs. M. A. Scovell, Chairman, Lexington, Ky., W. M. Allen, Raleigh, N. C., E. H. S. Bailey, Lawrence, Kansas, H. E. Barnard, Indianapolis, Ind., Richard Fischer, Madison, Wis., J. Hortvet, St. Paul, Minn., M. E. Jaffa, Berkeley, Cal., E. F. Ladd, Agricultural College, N. D., Floyd W. Robinson, Lansing, Mich., Jas. H. Shepard, Brookings, S. D., and Chas. D. Woods, Orono, Me. Dr. Chas. A. L. Reed, of Cincinnati, Chairman of the Legislative Committee of the American Medical Association, then read a paper on "Some Queries Suggested by the Referee Board on Benzoate of Soda," in which he criticized the methods employed by the Board, claiming that dietaries were selected of a nature specially adapted to add weight to the subjects experimented on, and suggested that the experiments were conducted by subordinates not under the immediate supervision of the members of the Board. Doctors Remsen, Chittenden and Long made further remarks in reply to Dr. Reed and ended the discussion. A paper was read by Dr. D. R. Lucas, of Columbia University, on "Some Effects of Sodium Benzoate." A resolution was then introduced to place the Association on record as endorsing the findings of the Referee Board. The discussion that followed developed the fact that two sides were sharply drawn on this issue, the resolution barely passing by the preponderance of one state, the vote being 57 to 42.

On Thursday afternoon the following papers were read:

The Chemistry of Bleached Flour, by Dr. H. W. Wiley, Chief Bureau of Chemistry, Chairman Food and Drug Inspection Board, U. S. Department of Agriculture, Washington, D. C.

The Need of State Laws to Protect the Consumers' Meat Supply, by Miss Alice Lakey, Chairman Food Committee, National Consumers' League, Cranford, N. J., read by Mrs. Florence Kelley, Executive Secretary, National Consumers' League, New York.

Organization and Work of the U. S. Branch Food Laboratories, by Dr. W. D. Bigelow, Chief of Division of Foods, Bureau of Chemistry, Department of Agriculture, Washington, D. C.

An address was also made by Wm. Hudson, of Michigan, representative of the National Wholesale Grocers of the U. S.

On Friday morning papers were presented as follows:

Soda Fountain Syrups and Crushed Fruits without Preservatives, by W. P. Anderson, Secretary, J. Hungerform Smith Co., Rochester, N. Y.

The Preparation of Condiments without Preservatives, by Chas. F. Louden, President, the Louden Packing Co., Terre Haute, Ind.

The Advance toward Higher Food Standards, Some Helps and Some Hindrances, by L. S. Dow, of H. J. Heinz Co., Pittsburg, Pa.

Some Important Facts Worthy of Consideration, by A. F. Merrell, President the Oyster Growers and Dealers' Association of North America, New York.

By resolution adopted on a previous day, the discussion on the controversial whiskey question, due for Friday's session, was omitted.

Friday afternoon was devoted almost entirely to the election of the following officers:

George L. Flanders, N. Y., President.
L. P. Brown, Tenn., 1st Vice-president.
D. Harvey Dillon, La., 2nd Vice-president.
Andrew French, Minn., 3rd Vice-president.
W. M. Allen, N. C., Secretary.
James Foust, Penn., Treasurer.

EXECUTIVE COMMITTEE.

C. D. Woods, Me,
S. H. Crumbine, Kas.
A. N. Cook, S. D.

New Orleans was selected as the place of the next meeting.

The social features of the convention were most enjoyable. Besides the all-day complimentary mountain trip to Mt. McClellan already spoken of, at which, by the way, eatables, drinkables and smokables were liberally provided during the day, a sunset banquet was tendered delegates and guests on Thursday evening, at Lakeside, and an automobile trip around the city on Friday morning.

ALBERT E. LEACH.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

The twenty-sixth annual convention of the Association of Official Agricultural Chemists met at the Brown Palace Hotel, Denver, August 26–28, 1909. Seventy-five members and guests registered during the convention, which met at virtually the same time as the Association of State and National Food and Dairy Departments and in adjacent rooms of the same hotel. The main order of business was as follows:

THURSDAY, AUGUST 26.

MORNING SESSION.

Phosphoric Acid, W. F. Hand, Mississippi.

Nitrogen, C. H. Jones, Vermont.

Potash, B. B. Ross, Alabama.

Soils, S. D. Averitt, Kentucky.

Inorganic Plant Constituents, F. W. Robison, Mich.

Additional papers prepared by Messrs. Trescot, Fraps, Stevens and Withers were presented.

AFTERNOON SESSION.

Appointment of committees (constitution, resolutions, etc.).

Insecticides, C. C. McDonnell, Washington, D. C.

Water, J. K. Haywood, Washington, D. C.

Committee A on Recommendations of Referees, J. K. Haywood, Washington, D. C.

Reports of committees:

On Unification of Terms, R. J. Davidson, Blacksburg, Va.

On Fertilizer Legislation, H. W. Wiley, Washington, D. C.

On Testing Chemical Reagents, L. F. Kebler, Washington, D. C.

On Revision of Methods, J. K. Haywood, Washington, D. C.

FRIDAY, AUGUST 27.

MORNING SESSION.

Food Adulteration, H. E. Barnard, Indiana.

Colors, H. M. Loomis, Washington.

Saccharine Products, C. D. Howard, New Hampshire.

Fruit Products, C. B. Cochran, Pennsylvania.

Wine, Julius Hortvet, Minnesota.

Beer, H. E. Barnard, Indiana.

Distilled Liquors, L. M. Tolman, Washington, D. C.

Vinegar, R. W. Balcom, Tennessee.

Flavoring Extracts, E. M. Chace, Washington, D. C.

Spices, A. F. Seeker, New York.

Baking Powders and Baking Chemicals, E. C. Clark, Massachusetts.

Meat and Fish, F. C. Weber, Washington, D. C.

Fats and Oils, T. J. Bryan, Illinois.

Dairy Products, H. C. Lythgoe, Massachusetts.

President's Address (special order for 12 o'clock), W. D. Bigelow, Washington, D. C.

In addition to the regular program an address was presented by Hon. James Wilson, Secretary of Agriculture, and papers were read by Messrs. Barnard, Ross, Horne and Smith.

AFTERNOON SESSION.

Cereal Products, E. F. Ladd, North Dakota.

Vegetables, W. L. Dubois, New York.

Condiments Other Than Spices, H. E. Bishop, Indiana.

Cocoa and Cocoa Products; Tea and Coffee, A. G. Woodman, Massachusetts.

Preservatives, P. B. Dunbar, Washington, D. C.

Water in Foods, P. F. Trowbridge, Missouri.

Separation of Nitrogenous Bodies: Meat Proteids, P. F. Trowbridge, Missouri.

Milk and Cheese Proteids, G. E. Patrick, Washington, D. C.

Vegetable Proteids, R. Harcourt, Canada.

Committee C on Recommendations of Referees, A. L. Winton, Illinois.

Committee on Unification of Methods of Analysis of Fats and Oils, L. M. Tolman, Washington, D. C.

Committee on Standardization of Alcohol Tables, L. M. Tolman, Washington, D. C.

Papers were presented at this session by Messrs. Smith and Hiltner.

SATURDAY, AUGUST 28.

MORNING SESSION.

Dairy Products, J. M. Bartlett, Maine.

Foods and Feeding Stuffs, J. P. Street, Connecticut.

Sugar, Chemical Methods, A. H. Bryan, Washington, D. C.

Molasses Methods, A. P. Agee, Louisiana.

Committee B on Recommendations of Referees, F. W. Woll, Wisconsin.

Special Committees (resolutions, constitution, etc.).

Tannin, F. P. Veitch, Washington, D. C.

AFTERNOON SESSION.

Drugs and Medicinal Plants, L. F. Kebler, Washington, D. C.

Medicinal Plants, C. H. LaWall, Pennsylvania; H. H. Rusby, New York.

The officers for the coming year are as follows:

EXECUTIVE COMMITTEE, 1909-1910.

W. A. Withers, Raleigh, N. C., President.

F. W. Woll, Madison, Wis., Vice-President.

H. W. Wiley, Washington, D. C., Secretary.

ADDITIONAL MEMBERS.

James M. Bartlett, Orono, Me.

J. T. Willard, Manhattan, Kans.

The members of the Association enjoyed the same social features that were tendered to the Association of State and National Food and Dairy Departments, and in addition a complimentary smoke talk was held by the Western Association of Technical Chemists and Metallurgists in their honor.

The second International Congress for the Suppression of Fraud will be held under the auspices of the White Cross Society of Geneva, at Paris, during October, 1909. An elaborate program has been prepared which covers the following subjects: Food Stuffs, Chemical Products, Pharmaceuticals, Essential Oils and Aromatics, and Mineral Waters.

The Second International Road Congress will be held at Brussels, July 31 to August 6, 1910. The first congress was held in Paris during 1908. ALBERT E. LEACH.

RECENT PATENTS.

The following patents relating to industrial engineering chemistry are reported by C. L. Parker, solicitor of chemical patents, McGill Building, 908 G Street, N. W., Washington, D. C.:

926,352. Method of Purifying Coal-Gas and Collecting By-Products. THOMAS MCWATTERS, Hawkins Station, Pa. June 29, 1909.

The process consists in purifying coal gas and collecting in the by-products thereof, passing the gas at a temperature of 300° Fahrenheit or thereabout, through a washer and thereby reducing the temperature of the gas to a temperature sufficient to eliminate substantially all the tar from the gas, then lowering to and maintaining the gas at a temperature sufficient to prevent the ammonia present assuming gaseous form, and finally by a further reduction in temperature eliminate the lighter tar and the liquor containing the remaining ammonia.

926,413. Process for Oxidizing Atmospheric Nitrogen by Electricity. DEMETRIO HELBRIG, Rome, Italy. June 29, 1909.

This is a process of oxidizing atmospheric nitrogen by electricity in which compressed air is projected by two opposite nozzles arranged in line, against an arc produced between suitable electrodes, whereby two sheaves of flame are produced which spread out along the electrodes in a plane normal to the direction of the nozzles.

925,988. Process of Hardening Tantalum. WERNER VON BOLTON, Charlottenburg, Germany, a corporation of Germany. June 22, 1909.

The process consists in adding to tantalum 3 per cent. of silicon.

926,729. Manufacture of Producer Gas. WILLIAM J. CROSSLEY, Openshaw, Manchester, and THOMAS RIGBY, Fairfield, Manchester, England, July 6, 1909.

This is a process of manufacturing producer gas by subjecting the fuel to a primary combustion while being mechanically agitated, continuously and automatically passing the resultant coke to the gas producer proper and passing the primary products of combustion through the coke in the gas producer.

926,820. Refractory Material and Process for Producing the Same. CHARLES L. NORTON, Manchester, Mass., July 6, 1909.

The process consists in roasting a mixture of magnesium carbonate and a silicious sand until the carbonate is thoroughly calcined, mixing the calcined magnesium and sand with asbestiform fiber and hydraulic cement, adding water to the aforesaid mixture of solids in quantities sufficient to form a wet pulp, and then subjecting the pulp to pressure while hydration of the cementitious materials is in progress, expressing the surplus water and compacting the entire mass.

926,980. Process of Making Alloys. JOHN T. H. DEMPSTER, Schenectady, N. Y. July 6, 1909.

The process consists in melting a quantity of nickel with a decarbonizing agent in a clay lined crucible to reduce the carbon, adding iron and chromium in suitable proportions, then adding manganese and pouring the mixture before the manganese attacks the clay lining.

926,999. Process of Producing Digestible Substances from Keratin. CARL NEUBERG, Charlottenburg, Germany. July 6, 1909.

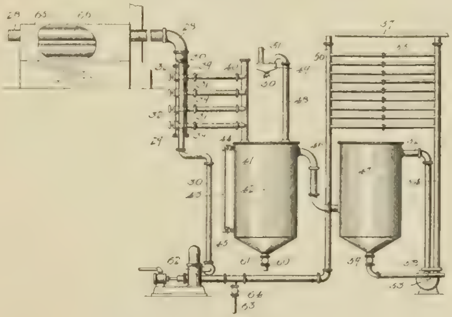
This is a process for converting keratin or keratin substances into digestible albumoses and peptones by subjecting keratin substances to the action of mineral acids for a time and at a temperature to transform the keratin until a diluted sample of the reaction liquid to which a precipitant for albumoses has been added after filtration shows no amino-acid nitrogen, whereupon the formed albumoses and peptones are isolated.

927,021. Process of Treating Arsenical Ores and Speiss. ANSON G. BETTS, Troy, N. Y. July 6, 1909.

This is a process of treating speiss by dissolving it as anode in a solution of a salt of a metal depositable more readily than hydrogen, while depositing said metal on the cathode and utilizing the full cathode effect of the current in metal deposition, and recovering metal of the speiss from the solution.

927,046. Method of Treating Ores. HASCAL A. HOGEL, New York, N. Y. July 6, 1909.

This process is designed for the treatment of refractory sulfid ores, more especially those containing sulfids of iron, lead, silver, and gold. The process depends upon the action of heat, sulfur, oxygen and salt. The process consists in subjecting the ores to the action of heat in the presence of air, mixing sulfur therewith (unless there is enough sulfur in the ore), mixing salt therewith, heating the mixture in the presence of air to a degree sufficient to volatilize the metals or other compounds which it is desired to recover



passing the volatilized products into a condenser containing a liquid, intimately mixing said volatile products with said liquid and with air, causing the liquid to repeatedly pass through the condenser, allowing the excess of air to escape from said liquid during its passage, cooling the liquid at one period of its passage through a part of said condenser, collecting the solid products deposited in said liquid, and treating the liquid and solid products to obtain the metals, lead, copper, silver, and gold in the usual way.

927,135. Process of Making Acetate of Lime. ROBERT W. ERWIN, St. Louis, Mo. July 6, 1909.

This is a process of making acetate of lime by evaporating a solution thereof in vacuum until the liquid reaches a specific gravity of substantially 1.08, continuing said evaporation in another vessel until the specific gravity of the liquid reaches substantially 1.12, further evaporating the liquid in an independent vessel until the specific gravity thereof

reaches substantially 1.16 or at the point of crystallization, and subsequently drying said crystals in vacuum.

927,198. Process for the Production of a Leather Substitute. RUDOLF WEEBER, Vienna, Austria-Hungary. July 6, 1909.

This is a process for producing a leather substitute by adding fibrous material to a solution of balata, caoutchouc and gutta percha, precipitating the agglutinant on to the fibrous material, separating the fibrous material from the solution, adding an oil to make the fibrous material soft and flexible, and forming said material into a sheet.

927,292. Method of Uniting or Welding Metals. WILLIAM S. SIMPSON, London, England. July 6, 1909.

This is a method of welding metals fusible at different temperatures, including iron or steel and copper, by subjecting the metals to heat at least equal to the fusing temperature of the metal that is fusible at the lower temperature and simultaneously subjecting the same to a carbonaceous material.

927,342. Process of Recovering Sulfur. WALTHER FELD, Zehlendorf, and ANTON JAHL, Honningen-on-the-Rhine, Germany. July 6, 1909.

This is a process for obtaining sulfur from sulphur dioxid and sulfuretted hydrogen by passing these gases through liquid having the power of dissolving the sulfur as it separates.

927,374. Process of Manufacturing Incandescent Mantles. ARTHUR MULLER, Furstenwalde-on-the-Spree, Germany. July 6, 1909.

The mantles are manufactured by impregnating the fabric of the latter with a colloidal solution of an oxid-hydrate of a rare earth.

927,418. Process of Manufacturing Gas from Wood. BURDETT LOOMIS, Hartford, Conn. July 6, 1909.

This is a process of making fixed producer gas from wood by placing in the base of a cupola a regulated body of hard carbon, then igniting and burning a body of wood on top of the hard carbon, drawing the resulting flame down through the hard carbon, and heating it to incandescence, feeding wood as required and drawing air down into the body of wood and drawing the resulting flame, hot gas and vapors down through said body of incandescent hard carbon, thereby converting the vapors and carbonic acid into fixed combustible gas.

927,457. Process of Bleaching. FRANZ FUHRMANN, Berlin, Germany. July 6, 1909.

The process consists in heating the goods to be bleached with a liquor containing magnesium perborate in presence of alkali salts of fatty acids.

927,495. Art of Producing from Foundry Iron a Product Having Cutting and Other Properties of High-grade Tool and High-speed Steel. EDGAR A. CUSTER, Philadelphia, Pa. July 13, 1909.

This is a process of producing tool and other metal from foundry iron, by chilling molten foundry iron in a permanent metal mold swiftly to the point of setting in a solid structure and thereafter chilling quickly in a fluid bath.

927,644. Process of Producing Oxids. HENRY L. DOHERTY, New York, N. Y. July 13, 1909.

The process consists in oxidizing moist finely divided iron by a current of air until the observed temperature begins to rise, replacing the air by a current of air diluted to carry less than the normal amount of oxygen, the dilution being directly as such observed tendency to rise in temperature and finally finishing by a current of air as temperatures begin to sink.

927,678. Preparation of Iron or Steel for Casting. PAUL RAKOWICZ, Griesheim, Germany. July 13, 1909.

This is a method of alloying iron or steel with magnesium by first passing iron or steel from the solid into a semifluid or thickly liquid state, then introducing magnesium into the thick mass.

927,758. Process of Treating Silicates of Aluminium for the Purpose of Obtaining Valuable Products. ALF SINDING-LARSEN, Christiania, Norway. July 13, 1909.

The process consists in feeding material containing aluminium silicate to one end of a long electric furnace and a mixture of iron and a reducing agent to the other end thereof, and passing an electric current between the electrodes extending into the furnace.

927,822. Manufacture of Lithographic Stone Artificially. THOMAS M. THOM, Woodlands, Cheshunt, England. July 13, 1909.

This is a process of manufacturing lithographic stone by powdering slag, mixing it with lime, molding the mixture into slabs and submitting the molded slabs to the action of carbonic acid gas gradually admitted thereto until the entire mass is hardened.

927,843. Process of Making Alloys of Zinc with Copper. STERLING ELLIOTT, Newton, Mass. July 13, 1909.

The process consists in producing an alloy of zinc with copper by first melting the zinc, then adding the copper to the molten zinc and raising the temperature to the melting point of the alloy which is to be produced, or thereabout, which is less than the melting point of the copper and also less than the boiling point of the zinc.

927,916. Process of Recovering Volatile Metals and Metalloids from Lead and Copper Slags. WILHELM WITTER, Hamburg, Germany. July 13, 1909.

The process consists in bringing the products or ores, when in a molten liquid state, into close contact with incandescent carbonaceous matter in the presence of an air current, consuming the carbonaceous matter for reducing the metals and metalloids to be recovered, and for maintaining the reduction and volatilization temperature, reoxidizing the reduced volatile metals and metalloids, and causing the so-formed oxids to escape with the current of combustion gases.

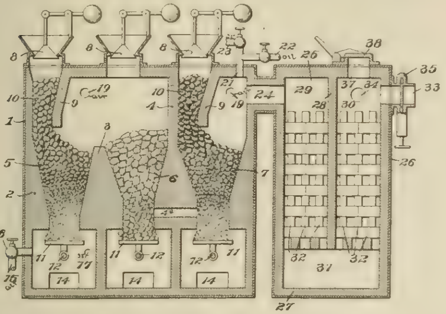
927,950. Process of Manufacturing Wood Pulp. CHARLES B. CLARK, Bangor, Me. July 13, 1909.

This is a process of digestively treating wood by the "sulfite process," so called, in a bath of digesting liquor contained in a digester to form wood pulp, by removing from the digester during the period of digestion an appreciable quantity of the bath containing resinous matters and extractives

of the wood for the purpose of recovering an appreciable portion of the bath after the passing of the resinous matters and extractives into it upon a resolution of the wood, and afterward continuing the process of digestion in the liquor left in the digester.

928,103. Process of Manufacturing Gas. B. BRAZELLE, St. Louis, Mo. July 13, 1909.

This is a process of manufacturing both fuel gas and illuminating gas by alternately admitting and cutting off a supply of air to a bed of hot coal, passing the products of combustion of such coal through a separate mass of mineral carbonates and thence through a second mass of coal, and thence through a mass of refractory material, and collecting



the fuel gas thus produced, and in passing the gas, which distils from the hot coal while the air supply is cut off through the mass of mineral carbonates and the second mass of coal, and then injecting volatile hydrocarbon into it and separately collecting the illuminating gas thus produced. The accompanying illustration shows apparatus in which the process is carried out.

928,235. Process of Making Patent-Leather or Artificial Patent-Leather. GEORGES R. DE MONTLORD, Boston, Mass. July 13, 1909.

The process consists in preparing a solution of nitrocellulose, a solvent, a vegetable oil, alcohol glycerin, spirits of turpentine, and a suitable pigment or dyestuff, immersing the leather or fabric into ethyl acetate, coating the surface of a glass-plate with one or more layers of the solution, uniting the leather or fabric with the coatings on the glass-plate by pressure, then drying the leather or fabric while on the glass-plate, and finally removing the coated leather or fabric from the glass-plate.

928,412. Method of Treating Armor Plates. SAMUEL S. WALES, Munhall, Pa. July 20, 1909.

The armor plate is produced by heating that face of the plate which is to be hardened to a hardening temperature, simultaneously artificially cooling the back of the plate, periodically interrupting the cooling action or effect, and controlling the length of each period of interruption.

928,476. Process of Manufacturing Silicon Nitrid. ALF SINDING-LARSEN, Christiania, Norway. July 20, 1909.

The process consists in producing vapors of silicon and causing the same to be acted upon by gaseous nitrogen in heated condition

928,512. Process of and Apparatus for Burning Cement and Like Materials. BYRON E. ELDRED, Bronxville, N. Y. July 20, 1909.

The process consists in mixing air with products of combustion and combustible gas in controlled proportions and causing the mixture to undergo combustion in proximity to pulverulent calcareous materials contained in a hot walled zone.

928,545. Process of Making Nitric Acid. FRIEDRICH L. SCHMIDT, Charlottenburg, Germany. July 20, 1909.

The process consists by causing sulfuric acid in molecular proportions to react on nitrate of calcium and separating the nitric acid thus obtained from the sulfate of calcium by filtration and afterward washing the sulfate of calcium with dilute nitric acid and water.

928,551. Method of Refining Iron. PAUL SEJOURNET, Paris, France. July 20, 1909.

The process consists in cooling low-carbon steel from a molten condition until it is at least in part solidified and the carbon therein has been oxidized by the contained oxygen and the oxid or oxids of carbon driven off, and remelting in the absence of carburizing conditions.

928,580. Process for Producing Incandescent Mantles. GEORG BUHLMANN, Gross-Lichterfelde, near Berlin. July 20, 1909.

This is a process for the impregnation of incandescent mantles consisting in dissolving a salt of an illuminating rare earth metal, adding to said solution a substance capable of reducing the acidity of said solution, shaking said solution in order to redissolve the precipitate, repeating the addition of the substance for reducing the acidity and shaking until the precipitate formed can no longer be dissolved and dipping the mantle fabric in the impregnating bath so formed.

298,734. Process for the Electrolysis of Alkali Chlorids. JEAN BILLITZER, Vienna, Austria-Hungary. July 20, 1909.

This is a process for electrolysis of alkali chlorids, by compelling a part of the cathode product to form a thin layer of the electrolyte and the constant removal of said layer as it is formed.

928,844. Manufacture, Concentration, and Simultaneous Purification of Sulfuric Acid. GASTON C. DE BRIAILLES, Paris, France. July 20, 1909.

This is a process of manufacturing sulphuric acid from sulphurous acid by electrolysis of a solution of sulphurous acid by keeping the solution at substantially the same specific gravity as the solution of sulphurous acid by adding the requisite quantity of sulphuric acid.

928,974. Process of Obtaining By-Products from Gases. GUSTAV HILGENSTOCK, Dahlhausen-on-the-Ruhr, Germany. July 27, 1909.

This is a process for obtaining by-products from gases of dry distillation of coal and other materials by dividing the first quantities of gases from the retorts or coke ovens, containing the greater part of the tar yield from the latter quantities of the gas from the retorts or coke ovens, containing relative little tar, removing the tar from the said first quan-

tities of gas and then combining the substantially tar-free gas so produced with the said latter quantities of the gas.

929,131. **Prepared Carbid of Calcium.** Zavier Herme. Fruitvale, California. July 27, 1909.

This product is produced by mixing one part of sugar and one hundred parts of carbid of calcium; then successively mixing with said substances one-fourth of one part of petroleum, one part of sugar, four and one-half parts of glucose, and two and one-half parts of sugar.

929,152. **Method of Making Cement, Mortar, and Concrete Water-tight.** Paul Mecke, Stettin, Germany. July 27, 1909.

The method consists in adding to the cement or lime mixture a pulp produced by the transposition of basic oleate of lime with sulfate of aluminium.

929,219. **Method of Treating Aluminous Materials.** Aldus C. Higgins, Worcester, Mass. July 27, 1909.

The method consists in fusing an aluminous material in an electric furnace at a temperature substantially above the state of quiet fusion and sufficient to prevent substantial segregation of impurities, and recovering the resulting product in solid form.

929,276. **Electrolytic Diaphragm and Method of Making the Same.** Anson G. Betts, Troy, N. Y. July 27, 1909.

This is a method of preparing asbestos board for use as a diaphragm in aqueous electrolysis, by cementing together the fibers of the board by means of an easily fusible substance insoluble in the solution in which the diaphragm is to be used.

929,383. **Process of the Manufacture of a Disinfectant.** Alexander Brick, Vienna, Austria-Hungary. July 27, 1909.

The process consists in mixing a soap solution containing alcohol with ethereal oils, adding formaldehyde to this mixture, heating this mixture combined with formaldehyde, allowing this mixture to cool, and adding to the cooled mixture incompletely saponified oils containing alcohol.

929,517. **Method of Treating Aluminum Ores.** Frank J. Tone, Niagara Falls, N. Y. July 27, 1909.

The process consists of making a mixture of aluminum silicate, emery and carbon, the amount of carbon being sufficient to reduce the silica and all compounds in the mixture except alumina, but insufficient to reduce the alumina, interposing this mixture as a resistance conductor between electrodes, passing current through the same sufficient to fuse the alumina and reduce the other constituents to metallic form and keeping the temperature of the charge below the reduction temperature of alumina.

929,518. **Process of Treating Aluminum-Silicate Ores.** Frank J. Tone, Niagara Falls, N. Y. July 27, 1909.

The process consists in forming a charge of aluminum silicate, base metalliferous material, and carbon, subjecting such charge to electrically developed heat, partially reducing the silica thereby, and alloying the reduced silicon with the reduced metalliferous material, then increasing the percentage of metalliferous material and subjecting the charge to sufficient electrically developed heat to fuse the alumina, reduce the silica and alloy the silicon with the reduced metalliferous material.

929,687. **Clad Metal and Process of Producing the Same.** John F. Monnot, New York, N. Y. August 3, 1909.

This is a process of producing clad metal objects comprising unlike metals weld-united, by casting molten bodies of unlike metals into contact with opposite surfaces of a separator of material capable of weld-uniting with both the metals so cast, and progressively cleaning one or both said surfaces by the action thereon of a deeper layer of cleansing material progressively displaced by the molten metals so cast.

929,726. **Method of Obtaining Purified Ammonia Gas from Ammonia Liquors.** Charles M. Stine, Chester, Pa. August 3, 1909.

The method consists in forcing a current of air through ammoniacal liquor, and gradually increasing the temperature of the same to a point at, or above, the boiling point of water.

929,845. **Art of Improving the Odor of Vegetable Oils.** John H. Filbert, Baltimore, Md. August 3, 1909.

This is a process of improving the odor of cottonseed oil, by mixing with the oil fresh animal crackling so as to imbue the oil with the essence, odor or flavor residing in the crackling, then separating the oil and crackling.

929,861. **Process for Obtaining Starch and Gluten from Wheat Flour.** Friedrich A. V. Klopfer, Leubnitz, near Dresden, Germany. August 3, 1909.

This is a process for separating large-grained and valuable starch from the albumen pulp containing the small-grained starch, the entire albumen, the soluble carbohydrates, and the soluble salts, by adding to the water while stirring it, together with the wheat flour to be centrifuged, chlorid of sodium in such small quantities up to one per cent. so that the gluten cellular texture is not dissolved, but only its structure loosened, whereby, after the mixture is finally treated in a separator, the gluten, the starch and a wheat flour extract containing the extractive wheat flour substances soluble in water are obtained without destroying the lecithin bound to the albumen and the ferments of the flour.

929,925. **Art of Improving the Odor of Lard Substitutes.** John H. Filbert, Baltimore, Md. August 3, 1909.

The process consists in improving lard substitutes containing a stiffening fat and vegetable oil by imbuing the same with the essence of heated animal tissue.

929,962. **Manufacture of Lead Arsenate.** Ellerslie E. Luther and William H. Volck, Watsonville, California. August 3, 1909.

The process consists in heating white arsenic in contact with a suitable lead compound, and continuing the heating and roasting the combined material in the presence of oxygen.

930,028. **Method of Reducing Ores.** Frederick M. Becket, Niagara Falls, N. Y. August 3, 1909.

This is a method of reducing ores of refractory metals, by smelting a charge containing such ore and a borid, while maintaining therein a temperature sufficient to secure substantial elimination of the boron from the reduced product.

930,057. Process for Making White Lead. JOHN A. ERBSLOW, Los Angeles, Calif. August 3, 1909.

The process consists in causing lead in divided condition to pass alternately into a body of water and of gas containing carbon dioxid and oxygen, to cause corrosion and attrition of the lead and to form a foam containing white lead, drawing off said foam and drying the foam to obtain white lead.

930,274. Method of Treating Wood during Distillation. HOWARD W. DOUGHTY, Amherst, Mass. August 3, 1909.

The process consists in hydrolyzing the cellulose with sulfuric acid and steam under pressure and driving off the volatile oils by the same heat, treating the solid residue with sodium hydroxid and after filtering bringing the acid and alkali solutions together in equivalent proportions, whereby the sulfuric acid is neutralized and the resinous acids are precipitated, then filtering, fermenting the filtrate and distilling off the alcohol.

930,344. Process of Treating Titaniferous Iron Ores. WILHELM BORCHERS, Aix-la-Chapelle, Germany. August 10, 1909.

The process of treating titaniferous iron ores, consisting in initially smelting such iron ores in presence of carbon directly, drawing off the crude iron, reducing the slag produced during the smelting operation by carbon to a reducing agent, and utilizing said reducing agent for reducing subsequent charges of titaniferous iron ores.

930,376. Method of Treating Aluminous Materials. ALDUS C. HIGGINS, Worcester, Mass. August 10, 1909.

This is a method of treating artificially prepared aluminous materials by subjecting such materials, suitably subdivided, to heat under oxidizing conditions, and thereby oxidizing impurities therein.

930,442. Method of Making Acids. JOHN L. TUFTS, Boston, Mass. August 10, 1909.

This is a continuous method of producing volatile acids by commingling a salt of such acid and an acid body capable of decomposing the same, working the mixture under the influence of heat until portions of the same become solid, continuously displacing such solid portions from the remaining pasty portions, continuing the working of said pasty portions and subjecting the displaced solid portions to the action of heat.

930,471. Process of Manufacturing Sulfuric Acid. WILLIAM HALLOCK, New York, N. Y. August 10, 1909.

The method consists in subjecting sulfurous oxid to the influence of an ionizing agent in the presence of oxygen.

930,575. Process Relating to Refractory Substances. ROBERT TRIPMACHER, Schweidnitz, Germany, August 10, 1909.

This is a process of binding refractory substances by treating the same in pulverized condition with a liquid which consists in a saccharine solution, and a boron and a chromium compound, in which naphtha is emulsified.

930,666. Process of Treating Ores. PAUL L. T. HEROULT. La Proz, France. August 10, 1909.

This is a method of treating copper ore containing sulfur which consists in feeding it into an electric furnace and passing it gradually through a zone of fusion in said furnace, and simultaneously injecting oxygen into the ore above the zone of fusion to oxidize part of the sulfur.

930,697. Waterproof Cement and Method of Making the Same. JACOB F. SCHOELLKOPF, Buffalo, N. Y. August 10, 1909.

The cement comprises a mineral cement and an insoluble resin salt of lime uncombined with material foreign to the base of said salt.

930,723. Process of Forming Electric-incandescent Lamp Filaments. WERNER VON BOLTON, Charlottenburg, and FELIX HARTMANN, Berlin, Germany. August 10, 1909.

The process consists in fitting into a tube of ductile metal a tube of a different, very ductile metal, inserting tungsten powder into the latter tube, subsequently working the tubes and the tungsten powder into filamentary form, removing the outer tube, and subsequently removing the inner tube from around the tungsten metal.

930,764. Method of Treating Iron Ore. JOHN T. JONES, Iron Mountain, Mich. August 10, 1909.

The method consists in mixing carbonaceous material therewith, then advancing the mixture through a highly heated non-oxidizing atmosphere, to consume the carbonaceous material and support its combustion with oxygen from the ore, thus reducing the ore, then advancing the reduced mass through a still more highly heated non-oxidizing atmosphere to fix the metal constituent without melting the slag-making constituents.

930,801. Method of Manufacturing a Porous Material. HERMANN SENN, Szczakowa, and DAVID KLUGER, Trzebinia, Austria-Hungary. August 10, 1909.

This is a method of manufacturing a porous material which consists in calcining slate containing small quantities of organic substances whereby the material swells and assumes a cellular structure and becomes suitable for use as an insulating and filtering medium.

930,815. Electrolyte. ABRAHAM VAN WINKLE, Newark, N. J. August 10, 1909.

This is a zinc electrolyte containing fluosilicate of zinc, and a salt of aluminum.

930,874. Cellulose Substitute. OSCAR MULLER, Cologne, Germany. August 10, 1909.

The material consists of cottonseed shells from which the binding materials, dye substances and cotton fibers have been eliminated.

930,909. Process of Making Extracts. WILHELM WIEGAND, Mersburg, Germany. August 10, 1909.

This is a process for drawing extractive matter from different materials such as tannic material, dye-wood, beet and like by advancing the solid material in a horizontal direction from one end of a horizontal elongated receptacle and the liquor from the other end, permitting the liquor to enter said receptacle in such a manner that the solid material will always stand at a higher level than the liquor, and stirring the material in a vertical direction while feeding it in a horizontal direction, whereby those parts which first

lie beyond the level of the liquor are dipped into it, and other parts are raised out, no mixing of the strata of liquor of different degrees of concentration being effected thereby.

930,968. Process of Obtaining Pure Metallic Copper from a Solution of a Salt of Copper. LUCIEN JUMAU, Paris, France. August 10, 1909.

The process consists in obtaining pure copper from a solution containing salts of copper by subjecting said solution to heat and pressure in the presence of a suitable quantity of wood used in any form, such as sawdust, shavings, waste wood and the like.

930,976. Composition of Matter. SAMUEL A. LEAVITT, Gorham, N. H. August 10, 1909.

This is an expansile acid-proof cement for lining digesters or the like, consisting of litharge, quartz, calcined plaster and lampblack, all brought to a plastic condition by the admixture of glycerin.

931,015. Insulating Composition. MINDELIN McGERRY, Kalamazoo, Mich. August 10, 1909.

The composition consists of asbestos pulp, slippery elm, a vegetable acid, glue and starch dissolved in water and cooked to a paste.

OFFICIAL REGULATIONS AND RULINGS.

FOOD INSPECTION DECISION 109.

THE LABELING OF WINES.

On June 30, 1909, a hearing was held before the Secretary of Agriculture and the Board of Food and Drug Inspection on the labeling of Ohio and Missouri wines. After giving full consideration to the data submitted, the board is of the opinion that the term "wine" without modification is an appropriate name solely for the product made from the normal alcoholic fermentation of the juice of sound ripe grapes, without addition or abstraction, either prior or subsequent to fermentation, except as such may occur in the usual cellar treatment for clarifying and aging. The addition of water or sugar, or both, to the must prior to fermentation is considered improper, and a product so treated should not be called "wine" without further characterizing it. A fermented beverage prepared from grape must by addition of sugar would properly be called a "sugar wine," or the product may be labeled in such a fashion as to clearly indicate that it is not made from the untreated grape must, but with the addition of sugar. The consumer is, under the Food and Drugs Act, entitled to know the character of the product he buys.

Evidence was offered on the preparation of "wine" from the marc. In these cases it appeared customary to add both water and sugar to the marc and sometimes to use saccharin, coloring matter, preservatives, etc., to make a salable article.

In the opinion of the Board no beverage can be made from the marc of grapes which is entitled to be called "wine" however further characterized, unless it be by the word "imitation." The words "Pomace Wine" are not satisfactory, since the product is not a wine in any sense, but only an "imitation wine" and should be so labeled.

H. W. WILEY,
F. L. DUNLAP,
GEO. P. McCABE,
Board of Food and Drug Inspection.

Approved:
W. M. HAYS,
Acting Secretary of Agriculture.
WASHINGTON, D. C., August 21, 1909.

JUDGMENT NOS. 83-91 FOOD AND DRUGS ACT.

83. Misbranding of wine (fermented solution of commercial dextrose, artificially colored and preserved with benzoic acid).
84. Misbranding of baked beans and tomato sauce (underweight).
85. Misbranding of canned tomatoes (underweight).
86. Misbranding of a drug product (saltpetre).
87. Misbranding of evaporated apples (as to quality).
88. Adulteration of milk (added water).
89. Misbranding of evaporated apples (underweight).
90. Misbranding of canned peas (underweight).
91. Misbranding of lemon, raspberry and strawberry extracts.

(T. D. 29941.) *Drawback on Aluminium Ingots.*

TREASURY DEPARTMENT, August 6, 1909.

SIR: The Department's regulations of November 10, 1906 (T. D. 27697), providing for the allowance of drawback on aluminium sheets, bars, plates, and tubing manufactured by the Pittsburg Reduction Company, of Pittsburg, Pa., wholly from imported aluminum in the pig, are hereby extended, so far as applicable, to cover aluminum ingots manufactured by the Northern Aluminum Company (Limited), of New Kensington, Pa., from imported crude aluminum, in accordance with the sworn statement dated April 3, 1909, transmitted herewith for filing in your office.

In liquidation, the quantity of imported crude aluminum which may be taken as the basis for the allowance of drawback may equal the quantity used as declared in the drawback entry, after official verification of exported quantities, provided it shall not exceed the net weight of the exported material with an addition thereto for worthless waste not to exceed 1 per cent. of such waste.

Respectfully,
JAMES B. REYNOLDS,
(63567.) *Assistant Secretary.*
COLLECTOR OF CUSTOMS, Philadelphia, Pa.

ERRATA.

July number, page 476, second column:

In the heading read: "The Determination of Zinc," instead of "The Determination on Zinc."

Line 9, from bottom, page 476, read: "heated to faint redness," instead of "heated to redness."

Line 8 from bottom, page 476, read: "cooled," instead of "colored."

Footnote 1, page 456, read: See Waring on precipitation from formic acid solution, instead of See Waring, "On Precipitation from Formic Acid Solution."

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ORIGINAL PAPERS.

THE CHEMICAL EXAMINATION OF ASPHALTIC MATERIAL.

By S. W. Parr, Brainerd Mears and D. L. Weatherhead.

Received August 2, 1909.

The asphalt products of the United States have increased in value from six hundred and seventy-five thousand dollars in 1898 to nearly three million dollars in 1907, and the accompanying increase in the use of material by municipalities, together with the fact that the substances are mixtures and offer temptation for adulteration, has led to frequent demands for ratings and analyses. On attempting to comply with these requests, we have encountered serious obstacles. Most of the specifications for contracts and methods of analysis have been worked out and depend upon the presence of Trinidad asphalt in the product, and seem to be unsuited for the mixtures prepared in the middle and western part of the United States. These very frequently contain gilsonite tempered with petroleum residues of either an asphaltic or paraffine base, or both, and, while often not complying strictly with the specifications, are undoubtedly good mixtures for the purposes for which they are prepared.

Setting aside the physical tests, which are of great importance and which must be made in judging any asphaltic mixture, and turning our attention to those methods which are based on extractions with organic solvents and which are intended to give light on the quantity and properties of the chemical constituents, we find the methods in use most unsatisfactory. They are time-consuming, expensive and, owing to the changing specific gravity of the solvents used, do not furnish the concordant results desired. It accordingly seemed necessary, despite the numerous efforts of other investigators, to improve, if possible, the method of attack at this point.

In 1907, Mr. W. H. Leverette, working in this laboratory, started on a plan of analysis differing from the older methods of extraction, the principle being to dissolve the bitumen as completely as possible and successively precipitate out the significant portions with partial solvents. It is along this line of procedure that the following investigations have been carried on.

EXPERIMENTAL.

With a view of obtaining the most complete solvents, experiments were carried out on a sample of practically ash-free gilsonite with chloroform, carbon disulphide, carbon tetrachloride, hot turpentine, benzol and toluol. From these, carbon disulphide was selected as the most suitable. After considerable experimentation, the method resolved itself into the following procedure: Half-gram samples of the powdered gilsonite are placed in separatory funnels of about two hundred and twenty-five cubic centimeters capacity and dissolved in five cubic centimeters of carbon disulphide. When complete solution has taken place, one hundred cubic centimeters of hexane (sp. gr. 0.6516) are added which precipitates a substance termed Precipitate No. 1, and which corresponds

to the "Asphaltene" of the usual methods. After standing two hours the mixture is filtered on a specially prepared Gooch crucible, which is dried in an air bath to constant weight at 105° C. This procedure was permissible as experimentation showed that no oxidation of the precipitate took place. The precipitate calculated to percentage of the sample was termed Precipitate No. 1.

Experiments carried on with freezing mixtures and also tests to determine the effect of boiling on the hexane mixture were found unsatisfactory, as precipitation seemed incomplete and variable under these conditions. Shaking and standing longer than two hours before filtering were shown to have little beneficial action.

In obtaining Precipitate No. 2, the filtrate from the preceding determination is evaporated to dryness in a separatory funnel on a water bath, the hexane recovered by condensation, and the residue taken up with ten cubic centimeters of the same. This hexane solution was then allowed to flow slowly into three hundred cubic centimeters of methyl alcohol, with constant stirring. Other solvents, such as a mixture of acetone and methyl alcohol, were tried, but methyl alcohol proved the most satisfactory. When the precipitation is complete the mixture is filtered on one of the specially prepared Gooch crucibles referred to above and dried at 105° C. As some of the precipitate adheres to the beaker, it is dissolved in five to ten cubic centimeters of hexane or toluene, transferred to a small glass dish, dried at 105° C. and weighed, the gain in weight of the crucible and the dish together representing the second precipitate.

Precipitate No. 3 was obtained by evaporating the methyl alcohol from the second determination and weighing the residue in a glass dish.

With a view of ascertaining the value of asphalt products and also to afford a means of comparison with other methods of analysis, the following substances were analyzed: Refined gilsonite; a petroleum residue called "Sarco Petrolene;" a mixture of equal weights of the same; a mixture of three parts "Sarco Petrolene" and one of the gilsonite; a mixture of two parts "Sarco Petrolene" by weight and one of gilsonite; a light cementing pitch; a mixture of equal parts of this pitch, "Sarco Petrolene" and gilsonite; a sample of Trinidad Lake Asphalt cement and a pure coal tar pitch.

The material obtained as Precipitate No. 1 from each substance analyzed, excepting the coal tar pitch, had the same physical properties. With this exception, they were all solid at 105° C. and could be easily powdered when dry. The precipitate from the coal-tar was more or less gummy at room temperatures and readily melted at 105° C. Precipitate No. 2, in the case of gilsonite, was sticky and soft at 105° C. From the other asphaltic samples it was sticky at room temperature and flowed at 105° C. In the case of the coal-tar there was no precipitate for No. 2. Precipitate No. 3 had the appearance of machine oil, but was more viscous.

The following tabular results of analysis were obtained:

TABLE I.—GILSONITE.

Sample	Ppt. No. 1 Per cent.	Ppt. No. 2 Per cent.	Ppt. No. 3 Per cent.	Total Per cent.
1	48.17	39.21[1]	10.09	97.47[1]
2	47.64	42.62	9.14	99.40
3	45.64	43.67	11.30	100.61
4	47.18	42.92	9.88	99.98
Average	47.16	43.07	10.10	99.99

TABLE II.—"SARCO PETROLENE."

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt No. 3. Per cent.	Total. Per cent.
1	3.07[1]	69.92	27.94	100.63
2	7.64	69.70	22.23	99.66
3	5.49	77.01	18.11	100.61
4	7.53	71.63	20.41	99.57
5	7.95	83.81	9.18[1]	100.44
6	4.90	75.44	19.04	99.38
7	7.50	82.32	9.65	99.47
8	6.93	72.15	20.51	99.59
Average	6.85	75.15	19.71	99.92

TABLE III.—MIXTURE 1.

Sample	Ppt. No. 1. Per cent	Ppt. No. 2. Per cent	Ppt. No. 3. Per cent.	Total Per cent.
1	27.48	52.16	20.48	100.12
2	27.29	53.03	19.64	99.96
3	29.20	50.20[1]	16.42	95.82[1]
4	29.48	54.83	16.92	101.23
5	29.40	56.03	14.88	100.31
6	29.38	50.86	19.52	99.76
Average	28.71	33.38	17.97	100.28
				100.06

TABLE IV.—MIXTURE 2.

Sample	Ppt No. 1 Per cent	Ppt No. 2 Per cent	Ppt No. 3 Per cent	Total Per cent
1	17.83	70.49[1]	12.29	100.61
2	18.58	67.87	13.66	100.11
3	17.77	63.06	19.05	99.88
4	19.02[1]	59.37	22.15	100.54
5	18.71	65.59	16.86	100.16
6	18.52	66.39	14.36	99.27
7	18.28	56.92	25.77	100.97
Average	18.28	64.46	17.22	100.22
				99.96

[1] Omitted from the average.

J. of Ind. and Eng. Chem., by B. Mears, Vol. I, 477.

TABLE V. MIXTURE 3

Sample	Ppt. No. 1. Per cent.	Ppt No. 2. Per cent	Ppt No. 3. Per cent	Total. Per cent.
1	20.03	.	..	
2	20 92	64 45	14 21	99 58
3	20.24	64.30	16.01	100.55
4	21.85[1]	63.59	14.73	100.17
Average	20 40	64 11	14 98	100 10
				99.49

TABLE VI.—CEMENTING PITCH.

Sample.	Ppt No 1 Per cent	Ppt No 2 Per cent	Ppt No 3 Per cent	Total. Per cent.
1	18.63	39.54	17.17	75.34
2	18 78	40 38	26 72	85 88
3	19.06	40.69	22.69	82.44
Average	18.82	40.20	22.19	81.22
				81.21

TABLE VII.—MIXTURE 4.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt No. 3. Per cent.	Total. Per cent.
1	26.29	45.08	24.60	95.97
2	27.74	51.45	16.39	95.58
3	26.38	48.10	22.15	96.63
4	24 13	50 43	22 04	96 60
Average	26 13	48 76	21 30	96 19
				96 19

TABLE VIII.—MINERAL MATTER IN TRINIDAD LAKE ASPHALT CEMENT

Sample	Per cent ash
1	27.74
2	25 59
3	25 07
4	24 28
Average	25.69

TABLE IX.—TRINIDAD LAKE ASPHALT CEMENT

Sample.	Insol in CS_2 Per cent.	Non bit[1] org. matter by diff Per cent.	Ppt No 1. Per cent.	Ppt. No 2 Per cent.	Ppt No 3 Per cent.	Total Per cent.
1	29 89	4 20	16.96	39 44[1]	13 94[1]	100 23
2	28 82	3 13	18 99	33 19	18 67	99 67
3	23 94	..	18 81	36.82	20 56	100 13
4	27 21	1.52	16.04[1]	32 86	23 84	99 95
5	25.14	..	18 96	30 71	25 71	100 52
Average	27 00	..	18 43	33 39	22 20	100 10
						101.02

TABLE X.—TRINIDAD LAKE ASPHALT PRECIPITATES CALCULATED TO PERCENTAGES OF MATERIAL SOLUBLE IN CARBON DISULPHIDE

Sample.	Ppt. No 1 Per cent	Ppt. No 2 Per cent	Ppt. No 3 Per cent	Total Per cent
1	24.09	55.99[1]	19.79[1]	99.87
2	26.54	46.38	26.04	98.96
3	24 73	48 41	27 05	100 19
4	22.03	45.15	31.90	99.08
5	25.32	41.02[1]	34.94[1]	99.08
Average	24.54	46.64	28.33	99.75
				99.51

[1] Omitted from the average.

TABLE XI.—COAL TAR PITCH.

Ordinary coal tar direct from tar-well concentrated by heat to soft pitch.

Sample	Insol. in CS_2	Ppt. No 1	Ppt. No 2	Ppt No. 3 by diff.
1	28.88	...	..	..
2	28.76	20.96	None	50.28
3	28.64	21.09	None	49.27

Precipitate No. 1 softens at 100° C. and melts at 105° C.

Gilsonite furnishes the highest percentage of Precipitate No. 1 and the lowest percentage of Precipitate No. 3 of any sample analyzed; while "Sarco Petrolene," an oil refinery residue used in tempering asphaltic material, gives the lowest percentage of Precipitate No. 1 and the highest of Precipitate No. 3. By taking the average of the percentages of the three precipitates obtained from gilsonite and the tempering oil we get, theoretically, the percentage composition of Mixture No. 1. A comparison of the percentage by analysis and the theoretical percentages is given below:

MIXTURE No. 1.

	Ppt. No 1. Per cent.	Ppt. No 2 Per cent	Ppt. No 3 Per cent	Total Per cent
Theoretically	27.00	59.11	14.90	101.01
By analysis	28 71	53 38	17 97	100 06

Though the actual analysis does not exactly agree with the theoretical, yet the same general division of the constituent hydrocarbons of the bitumen is seen.

MIXTURE No. 2.

	Ppt No. 1 Per cent	Ppt No. 2. Per cent	Ppt No. 3. Per cent	Total Per cent
Theoretically	16.93	67.13	17.31	101.37
By analysis	18.28	64.46	17.22	99.98

Again a general likeness is seen, although an exact agreement was not found. The comparison in the case of Mixture No. 3 is more favorable.

MIXTURE No. 3

	Ppt No. 1. Per cent.	Ppt No. 2. Per cent.	Ppt No. 3. Per cent.	Total. Per cent.
Theoretically	20.28	64.46'	16.51	101.25
By analysis	20 40	64 11	14 98	99 49

In this case a better agreement is obtained and shows that if the percentage composition, according to this method of analysis, of the hard bitumen and the tempering oil were known the proportions used for tempering could be estimated with a fair degree of accuracy. It must be borne in mind, however, that in melting together these mixtures to make a homogeneous compound, volatile products were given off which probably contained some of the

lighter constituents and may account for some of the discrepancies in the comparison.

From the data obtained on Trinidad Lake asphalt it seems that this method applies to this natural bitumen as well as to the artificial asphalts. Moreover, a comparison of the results obtained for Mixture No. 4 with those for the Trinidad Lake asphalt shows a sufficiently close agreement to expect of them similar qualities. Determination was therefore made of their flowing and melting points with results as follows:

Melting Points of Asphaltic Compounds.

	Softens.	Flows.	Sp. gr.
Trinidad Lake asphalt	65°	85°	1.201
Mixture No. 4, compounded of gilsonite, oil residue, etc.	68	80	1.015

These results, it will be seen, are quite consistent with the analytical data and make it evident that if the intrinsic qualities of these substances differ, the indication for that fact must be sought in a further examination of the fractions thus obtained by precipitation.

In the sample of coal-tar, the case stands very differently in that there is no second precipitate and in its yielding a first precipitate of such different properties from that found in the true asphalts as to make its detection a simple matter.

Much additional work needs to be done in the matter of the further examination of the various fractions to differentiate still further their properties, if indeed there are differences as between the various types of asphaltic compounds.

The method of separation as it now stands is no doubt susceptible of further improvement, but in its present state its advantages over the usual dissolving-out process are very pronounced. The use of hexane has been adopted because it is more nearly a constant compound than the heavier distillates. The amount of Precipitate No. 1 bears a direct relation to the specific gravity of the precipitating solution, a higher quantity being recovered with hexane than with ligroin, or the heavier distillates. While these latter are much cheaper, they vary not only from one lot to another, but frequently in the mere matter of handling, a modification in density will take place. For this reason the hexane is more satisfactory.

We wish to express our appreciation for materials furnished us gratuitously by the Standard Asphalt and Rubber Company, Barber Asphalt Company, and Standard Oil Company.

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University of Illinois,
Urbana, Illinois.

[Contribution No. 9 from The Research Laboratory of Applied Chemistry, Mass. Inst. of Technology.]

PAINT AND VARNISH COATINGS AS ACCELERATORS IN THE CORROSION OF METALS.

By William H. Walker and Warren K. Lewis.

Received July 1, 1909.

The packing of strongly acid fruits in tin cans has always been attended with more or less difficulty. A new method which has recently been developed for the protection of the can from the action of the fruit juices, is to lacquer the inside of the can with a high-grade copal-linseed oil varnish. The results are excellent so far as the preservation of the fruit is concerned, but an entirely unexpected difficulty has been met; namely, that the cans sometimes corrode through within a short time (six weeks or two months) after packing. An investigation of the nature of the varnish coating and the cause of its accelerating action on the corrosion of iron and tin has been carried out in this laboratory and has led to some very interesting results, which are the subject-matter of this paper.

The cans, placed at our disposal, were lacquered while still in the sheet, on one side, by a process analogous to that used in lithography. The lacquer was baked at 140–150° C. and the cans made up in the ordinary way from these sheets, the lacquered surface being inside. The interior of new cans was of a light, golden yellow color, and the coating to the eye was perfect in appearance. Cans which had been packed with strawberries for six to eight weeks were, however, badly corroded

on the interior. The corrosion was concentrated, mainly at the soldered joints, at those points where the die had crimped the ends, and along straight parallel lines down the sides of the cans. The action was extremely serious, the attacked areas being deeply eaten away, in some points the metal being corroded through, with a resultant leak.

While it is true that certain very acid fruits attack an ordinary can to a certain extent, it is no less true that under ordinary conditions the total corrosion, despite the fact that the available corroding surface is greater, is decidedly less than is the case in a lacquered can. It is impossible, then, that this corrosion of the lacquered can is due entirely to the acid of the fruits. The only new factor introduced is the lacquer itself and it must be that the lacquer in some way causes or accelerates corrosion. According to the electrolytic theory of the corrosion of metals, the rate of reaction can be increased only in three ways, either (1) by decreasing the concentration of the metal ion in the electrolyte in contact with the surface, (2) by increasing the concentration of the hydrogen ion about the cathodic area, and in these two ways increasing the driving force of the reaction, or (3) by lessening the polarization of the deposited hydrogen by the use of some effective depolarizing agent. The only way in which the lacquer could alter the ionic concentration of the two metals, tin and iron, involved, would be by their absorption and consequent elimination from the solution. It is in the first place extremely improbable that the lacquer should do this to any appreciable extent and then again we know that since the rate of corrosion of both these metals in pure water is so extremely small, that this absorption, even though complete, would have but a slight effect on the rate of reaction. That the lacquer should increase the acidity of the electrolyte materially above that due to the acids of the fruit juices is equally improbable, and, consequently, we are driven to the conclusion that it must be as a depolarizer that the lacquer exerts its influence. This is made the more likely by the fact that depolarization is by far the most effective means of accelerating the corrosion of metals in general. It must be that the lacquer renders the corrosion of the cans possible by the absorption and removal of the depolarizing hydrogen from the cathodic surface.

All protective films made from so-called drying oils owe their properties to the unsaturated nature of those oils and their consequent ability to absorb oxygen, transforming themselves thereby into substances such as linoxylin and related compounds. As is well known, this absorption is a slow one and the unsaturated state disappears completely only after the lapse of a great length of time, unless accelerated by the use of catalyzers (artificial driers), or by the increase of the reaction velocity through the use of higher temperature. Thus it is not only possible but frequent that such films even in use are still partly unsaturated. It is equally well known that unsaturated carbon compounds in general possess not only a capacity for absorbing oxygen, but hydrogen as well, and the unsaturated state can be relieved equally well by reducing agents as by the use of oxidizing materials. We know, however, that such compounds are capable of absorbing hydrogen only in the nascent condition; it is then not surprising if a linoxylin film, which is as yet not completely saturated, will absorb the polarizing hydrogen deposited when a metal such as iron or tin is brought in contact with an electrolyte.

To investigate the accuracy of these deductions the following experiments were performed: A U-tube containing KCl solution with an agar plug at the bottom, from which air had been carefully expelled, had inserted into one arm a lacquered electrode and into the other, one of bare iron, the two being connected externally. While blanks showed no test for iron whatever, when one electrode was lacquered with an oil and varnish film, a strong test for iron was obtained in the other arm of the U-tube. The corrosion was greatest with a linoxylin film; copal-varnish, cellulose nitrate, shellac, and asphalt followed in order, while lacquer baked sufficiently long at 250 C., as well as paraffine, showed no corrosion whatever.

In order to make sure that the corrosion was not due to small amounts of air which it might have been possible to remove from the agar plug in the bottom of the U tube, or which might condense on the walls of the glass which could not be heated up after the setting of the agar, the experiment was repeated in an apparatus which precluded the possibility of such an error. In a Mason jar, thoroughly steamed out for forty-eight hours before use, were placed two concentric, porous, porcelain cups and the whole three-fourths filled with water, which was boiled down to about one-third the volume of the jar. The electrodes were inserted into the boiling solution and the cap, through which lead a tube delivering hydrogen, was screwed on while

steam was still escaping at full force from the jar. Numerous experiments have shown that under these conditions, with bare electrodes, sufficient iron to be detected with ferricyanide is never obtained. If, however, a lacquered electrode was inserted into the outside compartment and a bare iron electrode in metallic contact with it into the inner cup, the inner cup invariably showed a strong test for iron after from eighteen to twenty-four hours. No iron could be detected in either the jar or the larger cup.

If such films accelerate corrosion, it must be made possible only by the flow of an electric current, and this current must be carried either by the conductivity of the film as such, or by the solution penetrating through its pores to the metallic surface beneath. The conductivities of such films were tested by measuring the resistance of a circuit consisting of a metallic conductor leading to two electrodes immersed in a U tube, the resistance being measured before and after coating with the film in question. The electrodes employed were short iron wires and the electrolyte a strong solution of calcium chloride. The vessel was a small U tube. The resistance of the circuit with bare electrodes was approximately 30 ohms. Lacquered electrodes increased the resistance to some 270 ohms but in the course of a couple of hours this value had fallen to about 80 ohms. In the same time, shellac presented a resistance of 70 ohms, cellulose nitrate of 80, linoxylin of 65, asphalt of 43, while paraffine electrodes offered a resistance so great that it could not be measured with the apparatus at hand. In other words, paraffine was impervious to the solution employed. By the addition of paraffine to the lacquer, its resistance could be increased to from 1500–3000 ohms, but the lacquer had become so brittle thereby that the practical use of such a film would be out of the question.

To show that the corrosion of the iron occasioned by the lacquer film is accompanied by the flow of an electric current through the external circuit, the following experiment was tried: A U-tube, as previously described, with a KCl solution and an agar plug, carefully boiled out, the whole under an atmosphere of hydrogen, contained two iron electrodes, the one bare and the other covered with a linoxylin film. An electrometer was inserted into the external circuit and the current flow measured as shown in the table below. It was found undesirable to use a silver voltameter for the excessively small currents employed and resort was had to a modification of Ostwald's Bromide Voltameter, described elsewhere in the Journal of this Society. This voltameter was used for all measurements made, after the first, which was done with the silver nitrate instrument.

Deposit obtained from current due to depolarization by two different linoxylin films.

	Time in hrs.	Deposit of mgs bromine.	Deposit mgs. per hrs.
Film No. 1	48	0.6	0.012
	76	1.0	0.013
Film No 2	41	1.8	0.044
	89	4.1	0.046
	185	8.7	0.047

These figures prove beyond doubt that the corrosion of the iron on the unlacquered side is due to the flow of an electric current through the external circuit from the lacquered surface.

These experimental facts seem to allow of but one explanation, namely, that the films in question are porous in their nature, allowing the electrolyte to penetrate them to the surface of the metal beneath, that some of these films, due to their unsaturated state, are capable of absorbing nascent hydrogen and in this way acting as depolarizers, and that aside from this, all the porous films allow the penetration through them to the surface beneath of any depolarizer that may exist in the solution, thus rendering the coated surface cathodic and concentrating the solvent action at the exposed part of the metal.

The reason for the failure of the fruit cans mentioned at the beginning of this article is now easily understood. While the lacquer film applied to the uncut sheet was probably a perfect one, still in the process of making the can, this film was ruptured at many points. Thus the die stamping out the head of the can broke the film at the place where the tin was bent; the mandrel, on which the body of the can was formed, scratched the sides in long parallel lines upon the removal of the can; and the burning of the joints destroyed the lacquer in their immediate neighborhood. When the fruit was introduced into the can, the depolarizing action of the lacquer itself, coupled with that of the small amount of air left in the can in packing, threw the protected areas into the cathodic state, concentrating the solution of the metal at the exposed points, dissolving in this way both tin and iron, and maintaining this corrosion until both the air was consumed and the unsaturated state of the lacquer was completely relieved. Before this point was reached, however, the corrosion

had gone far enough to seriously damage the fruit and even in many cases to puncture the can. This action is entirely independent of any possible imperfections in the tin plate. The remedy would be to find a lacquer impervious to the solution, or if that prove impracticable to at least furnish one which will not act as a hydrogen depolarizer. A non-porous lacquer it has as yet proven impossible to find; a saturated one can be made by sufficiently baking any ordinary varnish, but there still remains work to be done to develop this into a satisfactory solution of the problem.

It is self-evident, however, that the importance of these phenomena is by no means limited to the problem of lacquering fruit cans. The majority of protective coatings for iron contain linseed oil or some one of the various substances found by our experiments to be either unsaturated, or porous, or both; and so soon as a piece of metal painted with these substances comes in contact with water after the abrasion of the paint film at any point, all the conditions for corrosion as above outlined are fulfilled, and we may be sure that corrosion at the exposed point will be accelerated by the presence of such films in its neighborhood. It is true that the porosity of these films is reduced to a minimum by the use of the best obtainable loading materials, such for instance as certain pigments of ordinary linseed paints, the bituminous bodies of asphalt or coal tar paints, etc., and that these paints offer in consequence a much greater electrical resistance to the flow of the current than otherwise. One must not forget, however, that the insertion of such a resistance to the current flow can only reduce the rate of the reaction, and in no way influence its tendency or driving force. The exposure of such films to the air for a long period of time finally entirely saturates them, but this again does not affect their porosity and consequently does not preclude the possibility of acceleration of corrosion at the exposed point due to the depolarizing action of air through the film. These facts make clear the reason for the rapid deterioration and pitting of the iron or steel surface at points laid bare by the breaking down of many paint films and show why it is so exceedingly important that a metal surface should be clean and bright before the application of a paint.

If a paint or lacquer film be intact, despite the fact of its porosity, corrosion does not seem to take place at once beneath its surface. Thus an iron can, carefully painted with a high-grade varnish and filled with cold 5 per cent. sulphuric acid, showed a test for iron with ferricyanide first after twenty-four hours. If heated on the water bath, however, a test could be obtained in slightly over one hour, but even then the action was not severe. It may perhaps be that the electrolyte does not find sufficient continuous surface beneath the film to allow of a ready separation into cathodic and anodic areas. At any rate, corrosion does not readily take place if the film be intact, but the surface below the film does easily become cathodic if an exposed area in the neighborhood can act as anode. This cathodic liberation of hydrogen loosens the film from the metal in some way not yet clearly understood and likewise softens it. The resistance of a film diminishes quite rapidly in this way and it soon becomes weak and rotten and easily removable from the iron. It is easy to see how, especially with rough usage, exposed points in a painted steel surface rapidly grow in size.

A few of the common commercial paints and paint-making materials were examined, using the following apparatus: A glass U-tube of 1′ tubing with 6′ arms and 8′ in length over all, contains 200 cc. of normal KCl. The electrodes are of commercial soft iron wire, 0.044′ diameter carefully cleaned with emery. The bare electrode is 25 cm. long and the lacquered one 100 cm. The electrode is coated by dipping in the paint to be examined, the excess removed by rapid twirling and then dried. The water about the *cathode* is kept saturated with oxygen by bubbling air through it. The depolarization current is measured by the use of the bromide voltameter already mentioned. The bromide deposited is proportional to the time, up to a point when the film gives way. This point of disintegration is different for different films and two quantities can in general be measured, (1) the initial rate of depolarization

Paint film.	Corrosion in mgs. Bromine per hour.
"Durable metal coating"	0.70
"Copal linseed oil lacquer"	0.76
"Cosmos" (coal tar)	0.34
Graphite	1.87
Carbon black	2.4
Lampblack	2.3
Zinc chromate	0.11[1]
Barytes	1.2
Zinc oxide	0.078[2]
Graphite (baked)	0.078
White lead	0.10[3]
Linoxylin	0.31
Paraffine	0.00

[1] Broke down in 36 hours, but not badly.
[2] Still perfect after 71 hours.
[3] Broke down in 30 hours.

and (2) the time of rupture. This second factor is somewhat difficult to obtain because our voltameter measures not current but total amount of electricity passed, and it is frequently, if not usually, impossible to tell at exactly what point the increase in current began. In the above table is the average of the data obtained.

It is evident that the electricity measured by the bromine deposited is the resultant of a number of factors acting at the same time. A comprehensive study of the relationship between such data and the value of various paints as a protective coating for iron is now in progress.

THE CARTER PROCESS OF WHITE LEAD MANUFACTURE.

By J. S. Staudt.

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This company has two plants in the United States: one in Chicago, Ill., and the other in Omaha, Neb. The former has a capacity of about 20,000 tons annually and the latter of about 10,000 tons annually.

All descriptions and illustrations as herein given refer to the Omaha plant.

The lead bars or pigs, weighing about 95 lbs. each, are drawn up a chain elevator at the rate of 500 pigs per day, to be melted in a cast iron trough about 8 feet long, 18 inches wide and 12 inches deep, placed upon the second floor of what is called the "blow room." The lead is melted by means of a coal fire placed immediately below the trough.

On the side of the trough opposite the elevator is an opening through which pass two concentric tubes. The inner tube, nozzle shaped, serves for the passage of molten lead, and the outer for the passage of superheated steam. The tubes lead or open into a large iron compartment, about 33 feet long and 10 feet high, with a maximum depth of about 10 feet, tapering toward the base. Superheated steam is here produced by the same source of heat used in melting the lead, and is thus made as needed. It is the action of this superheated steam, blown against the molten lead, blowing it against the walls of the compartment, that reduces it into a finely divided state, granular and blue in appearance, called "blue lead."

The blown lead is not supposed to be oxidized before being put into the corroding cylinders. It will, however, undergo a slight oxidation when subjected to the moist air and the gases of the plant. When heaped up it will rise in temperature and become partly oxidized. Trap doors at the bottom of the iron compartment serve as means for the removal of the blown lead. The blown lead is removed by means of iron trucks, mounted on cast iron wheels, each truck holding about 4,000 lbs. Each truck is hauled upon an elevator and raised to the third floor. The contents are then dumped through an opening leading into a "corroding cylinder," on the second floor beneath. All the "corroding cylinders" are filled in this way, each "blue cylinder" receiving about 4,000 lbs. of blown lead. In the "corroding room" there are 69 "blue cylinders," as they are called, and 58 "white cylinders." The cylinders are made of wooden

Fig. 1.—Corroding cylinders.

planks 2 inches thick, are 10 feet long and 8 feet in diameter. Lead is kept in the "blue cylinders" for 10 days, 16 lbs. of acetic acid being added for three days. For the remaining seven days it is sprinkled with cold water by means of a hose, inserted through an opening in the end of the cylinder. This is done twice a day, once in the morning and once in the evening. The carbon dioxide enters the cylinder through a 2-inch pipe inserted through an opening in the axis of one end of each cylinder. The cylinders revolve very slowly, making one revolution in nine minutes. The function of the cylinders is twofold: first, it serves as a grinder in so far as the particles rub against each other while the cylinder revolves.

second, it serves to expose more lead to the corroding influences of acetic acid and carbon dioxide gas.

The corrosion is only partially completed in the "blue cylinders." The product is taken from these

Fig. 2.—Classifiers.

cylinders by means of vertical chutes, leading to trucks on the ground floor. Loaded trucks are taken by means of an elevator to the tower, dumped into a large hopper, leading into a mill grinding it into a fine powder. From this mill it leads into a large vertical chute 4 feet by 4 feet to the ground floor. Trucks are hauled under the orifice of this chute, filled with the ground product, and elevated to the third floor to be dumped into the "white cylinders." There are 58 "white cylinders" having the same dimensions and period of revolution as the blue. The product is removed from these through wooden vertical chutes, leading to the ground floor below, loaded upon trucks, elevated to the third floor where it is dumped through an opening in the floor into a chute leading to a grinding mill below the floor.

The ground white lead is then washed with water, passed through the classifiers, four of which are in the corroding room south of the mill. The classifiers serve the purpose of separating the coarse particles from the fine. Abundant water is used here so as to cause it to flow and at the same time wash it. The finest separation from the classifiers goes over the "shakers" where it is still further separated. The "shakers" consist of a framework covered with silk of very fine mesh. This framework is moved back and forth in a horizontal direction by means of a piston. The liquid white lead is fed upon the sieve by means of openings in the bottom of a trough at the head of the sieve. An operator regulates the flow by taking out or inserting wooden pegs fitting these openings. The part that goes through the fine silken sieve passes by the action of gravity through pipes slightly inclined to the "settling tanks" on the ground floor. The coarse from the four classifiers above referred to as well as from the "shakers" passes through conduits leading into a main which in turn leads through an opening in the axis of the north end of a pebble mill, also on the ground floor. Only one pebble mill is used. It is about 10 feet long and 4 feet in diameter, partially filled with pebble stones from 3 inches to 4 inches in diameter. From the axis of the south end of the mill the ground material escapes, passes through an inclined conduit into an adjacent bin from which it is pumped through a 2-inch pipe up to the two "classifiers" on the third floor. Here it is again separated into coarse and fine, the fine flowing through wooden conduits to the "shakers." The coarse from this having gone over the classifiers and through the pebble mill now passes through a revolving screen (silken), located on the ground floor. This separates the tailings—consisting of particles of wood, coarse white lead and uncorroded lead—from the good product which drops into a large bin below the revolving screen.

The tailings are sold for what the lead is worth for the making of litharge and red lead.

The "settling tanks" are 13 in number, arranged in two rows running north and south on the ground floor.

Fig. 3.—Pepper mill and settling tanks

The tanks are about 11 feet in diameter, and about 5 feet high, tapering toward the top. These tanks are filled with the fine product from the "shakers" diluted with plenty of water. The product as

it comes from the "white cylinder" is partly basic lead carbonate and partly lead acetate. Acetic acid acting on the lead forms basic lead acetate in the presence of air. The carbon dioxide acting on the basic lead acetate forms lead carbonate

Fig 4 -Drying pans

and lead acetate. This is the product that goes into the settling tanks together with a large quantity of water. Two bucketfuls of soda solution are added to each tank. This solution is made by dissolving 150 lbs. of Na_2CO_3 in one barrel of water. The sodium carbonate acting on the lead acetate changes it into lead carbonate. The contents of the "settling tanks" are agitated by means of an agitator, consisting of a wooden plank extending down into the basin with a cross piece at the end. Each tank is provided with an agitator. They are attached to horizontal shafts above each row, extending the full length of the rows and rotated back and forth by means of a piston rod. The white lead is kept in these "settling tanks" for about fifteen hours, agitated part of the time and then settled. The solution is tested for acetate or free acetic acid by a 10 per cent. solution of potassium iodide. After the contents of the basins are thoroughly settled the water is removed from holes, fitted with wooden pegs extending down one side of the tank. By the removal of these pegs the water can be removed to any desired depth. Great care is taken that the excess of soda is washed out of the precipitate since it saponifies with the oil which is later added. Phenolphthalein solution is used to test for the carbonate. The water thus removed is passed through an 8 foot sewer pipe to a "settling basin" about 75 feet east of the building. It consists of a hole dug out of the ground 18 feet by 7 feet and 10 feet deep, lined with concrete. Here a further precipitation of white lead, held in suspension by the water, takes place. The settlings from this basin are removed about once every three months.

Pure white lead now constitutes the settlings from the "settling tanks" which are removed through openings in the sides of the basins near the bottom, emptying into deep and wide wooden flumes, immediately below the floor. These flumes are inclined so that the white lead slowly flows into a bin below the floor at the north end of the room.

From this bin it is pumped through a 3-inch lead pipe into the "dry room" on the third floor at the north end of the building.

The "dry room" consists of two bins 100 feet long, one on the east side and one on the west side. These bins are provided with iron pans lined with copper, extending through the full length of the bins. The east bin contains five pans and the west bin four. Each pan has a double bottom. Steam circulates through the hollow thus provided, furnishing heat by which the white lead is dried. It requires about five days for the white lead in each pan to dry, in which state it cracks and breaks up into blocks very similar to mud drying in the

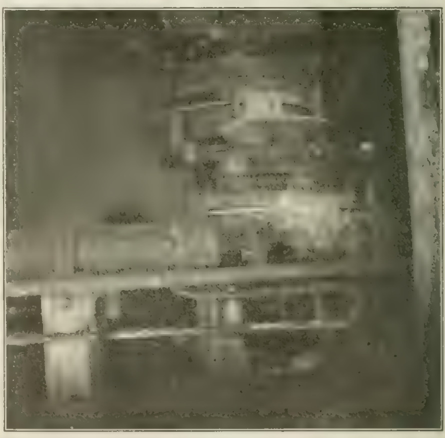

Fig. 5 Mixer.

sun. When dry it is removed by means of a shovel, passed through chutes to the room below called the "mixing room." Two mixing machines are in this room, one at the north end and another at

the south end. In these machines about 32 lbs. of linseed oil are mixed with 500 lbs. of white lead. Two kinds of linseed oil are used—boiled and unboiled. Boiled oil serves as a bleaching agent. The ratio of boiled to unboiled oil is approximately 1 to 1. "Pulp lead," *i. e.*, white lead which has never been, dried is also mixed with oil at the rate of 11 lbs. oil to 100 lbs. white lead. Some is mixed with oil by taking it one-half pulp and one-half dried. It is preferred this way by a great many painters. Again: a great deal is shipped without being mixed with oil at all, either as pulp, dried, or a mixture of the two.

From each mixing machine the white lead is conveyed by means of screw conveyors placed horizontally near the floor. At various intervals there are pipes passing through the floor to hoppers leading into machines on the ground floor in which the mixing is completed. A great deal of heat is generated in these machines due to the saponifying action of the oil on the $Pb(OH)_2$. The machines are kept cool by cold water circulating through conduits encircling the machines.

With these machines the Carter Process of White Lead Manufacture ends. From the exits of these machines it is packed into kegs varying in capacity from 12½ to 500 lbs. The daily output of the Omaha plant is about 32,000 lbs.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF MISSOURI.]

COMPOSITION OF THE FAT OF BEEF ANIMALS ON DIFFERENT PLANES OF NUTRITION.

(FIRST PAPER.)

BY C. R. MOULTON AND P. F. TROWBRIDGE

The present paper is a study of the changes effected upon the fats of beef animals when subjected to different planes of nutrition. In connection with the work on the flesh of steers and the influence of feed, breed, and age on the development of the various parts of the steer's organism and on the chemical composition of the same, which work is being carried on at the Missouri Agricultural College Experiment Station, it has been thought advisable to investigate the factors affecting the composition of the fats. Only the effects of condition and of resorption, with a slight reference to age, are considered here.

HISTORICAL.

The interrelation of the water and fat content of the animal body has been pointed out by Carl Voit.[1] He says in substance: In the case of bad nourishment the whole body becomes watery; a well-nourished organism contains on the contrary more dry substance since in it there is more fatty tissue with less water content. The effect of partial starvation has been studied by S. Hatai.[2] He noted that partial starvation gave a high per cent. of water and a low per cent. of ether alcohol extract in the central nervous system of albino rats.

M. A. Muntz[3] in his work with fat beef animals has shown that with fat animals the fat is very poor in the amount of solid fats, olein predominating to a great extent. Thin animals have a higher melting point and lower liquid fatty acid content.

Concerning the effect of situation in the animal body Victor Subbotin,[4] working with dogs, and M. A. Muntz,[5] working with the fat of sheep, have shown that the subcutaneous fats have lower melting points, lower content of palmitin and stearin, and higher content of olein than have the internal fats. W. Lummert[6] and v. Raumer[7] substantiate these results. V. Henriques and C. Hansen[8] draw the following conclusions from their work on various animals. The farther from the surface the lower the iodine value of the fat. The interior of the body is warmer than the surface and it seems possible that the temperature at which the fat is stored up in the body has an effect on its chemical composition. O. Lemmerman and G. Linkh[9] make similar observations.

The greater part of the work concerning the effect of age has been with the fats of human beings. The results lead to the conclusion that the melting point and solid fatty acid content decrease with age. König and Schluckebier[10] as the result of their work with pigs come to an entirely opposite conclusion. They state that the melting point of the fats increases with the age of the animal while the iodine values fall.

In Lawes and Gilbert's classical work the weights of fatty tissue are recorded but no work was done upon the composition of the fats. There is a deficiency in the amount of available data concerning the fats of beef animals.

[1] Herman's *Handb. d. Physiol.*, **6**, 1, 575 (1881).
[2] *Amer. Jour. Physiol.*, **18**, 309–320 (1907).
[3] *Comptes Rend. des Séances*, **90**, 1175 (1880).
[4] *Zeit. für Biologie*, **6**, 73–94 (1870).
[5] *Loc. cit.*
[6] *Pflueger Archiv*, **71**, 176–208 (1898).
[7] *Zeit. f. angew. Chemie*, **1897**, 210, 247.
[8] *Abstract, Jahresb. ü. Tierchemie*, **30**, 57 (1900).
[9] *Landw. Jahrb.*, **32**, 635–653 (1903).
[10] *Zeit. f. d. Unters. d. Nahr. und Genussm.*, **15**, 641.

EXPERIMENTAL.

The animals investigated were chiefly those used in the regular experiments of the Missouri Station.

Samples of fat from specific parts of the body of the steer were taken as the carcass hung in the cooler. All such samples were taken from the left side. The right half of the carcass was cut into the various wholesale cuts and a hand separation made of the lean, fat, and bone. After a thorough grinding and mixing samples were taken of the fats. In all cases a large enough sample was taken to allow for the determination of water, fat, nitrogen, ash, and phosphorus and to still leave a sufficiently large sample for rendering. The samples of fat were rendered on the hot water bath, squeezed through muslin, and then filtered through paper filters. The clear fats were collected in sample bottles and dried in a vacuum oven at 60° C. and a pressure of —60 cm. All of the samples were kept in cold storage at a temperature a little above freezing.

The fresh samples of fatty tissue—from two to four days old—were analyzed as follows:

Moisture Content.—The moisture content was determined by the Benedict vacuum method as further modified for use in this laboratory.[1]

Fat.—The thimbles from the above determination were placed in Soxhlet extractors and extracted for twenty-four hours with ether distilled from sodium. The ether remaining in the thimble was driven off at a temperature not to exceed 60° C. and the tubes were then dried in vacuum desiccators as per above. The loss in weight represented the fat content. The results were very satisfactory, the triplicates generally agreeing closely.

Protein.—Samples of from 3–5 grams were weighed out in triplicate into 9 cm. filter papers, rolled up in them, and transferred to 500 cc. Jena Kjeldahl flasks. They were then digested with sulphuric acid, using mercury and potassium sulphate. The ammonia was distilled off and determined in the usual manner, using tenth-normal hydrochloric acid and cochineal. The nitrogen found multiplied by the protein factor 6.25 gave the protein content.

METHODS OF INVESTIGATION FOR THE RENDERED FATS.

The rendered and filtered fats were kept in cold storage until they could be investigated. The tendency of the lower melting point fats to precipitate out the glycerides of the solid fatty acids on cooling was very noticeable. It was therefore necessary to melt the mass of rendered fat and mix it thoroughly. The containers were 50 cc. Erlenmeyer flasks stoppered with corks. It was thus easy to melt the sample by placing it in the air oven at 60° C. The sample was then mixed by rotating the flask and the portions for analysis were weighed out by difference while the fat was still melted. The last drop on the lip of the Erlenmeyer could be taken off by means of the cork stopper and returned to the flask. The fat was poured into the vessel used for analysis. The specific gravity, melting point, saponification value, and iodine value were determined. The methods employed were as follows:

Specific Gravity.—Sprengel tubes of 5–10 cc. capacity were made. Weighings were made of the empty tube, tube and water at 15° C., and tube and fat. The tubes were filled with fat at 100° C. and allowed to cool.

Melting Point.—This determination was carried out as per Wiley's official method as given in detail on page 133 of the Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists, 1907. A flat disc of fat is placed in an alcohol water mixture and gradually heated. The temperature at which the fat rolls up into a sphere is taken as the melting point.

Saponification Value.—The saponification value was determined as given in detail on page 137 of the Official and Provisional Methods.

Iodine Value.—The iodine value was determined by the method of Wijs. The procedure was as outlined on page 136 of the Official Methods excepting that Wijs' solution was employed and the details slightly modified to agree with the accepted practice when using a Wijs solution.

CONDITION AND AGE OF STEERS AT TIME OF SLAUGHTERING.

Manner of Feeding.

Steer No. 18 was a grade shorthorn three and a half years old. He was a thin animal on maintenance, being fed 2.5 parts of grain (8 cracked corn to 1 linseed meal) to 1 part of hay. His carcass graded as a "cutter."

Steer No. 121 was a grade shorthorn three and a half years old. He was a fairly fat animal on full feed, being fed the same kind of feed as No. 18.

[1] P. F. Trowbridge, November, 1908, Proceedings of the Association of Official Agricultural Chemists (U. S. Dept. of Agriculture. Bureau of Chemistry *Bulletin*, **122**), p. 215. I. F. Shackell, *American Journal of Physiology*, **24**, 325 (June, 1909).

He lacked sixty days of finish, but his carcass graded as number one.

Steer "Geordie" was a full blood Galloway two years old. He was a very fat show animal. His carcass was first-class beef but rather blubbery on the outside. He was fed grain 2 parts corn, 2 parts oats, 1 part bran, and 1 part alfalfa meal. He had alfalfa hay *ad libitum* and during the summer months he was on grass at night.

Steer No. 505 was a grade Hereford eleven months old. He was a fat animal on full feed, being fed 2 parts of grain (6 cracked corn, 3 whole oats, 1 linseed meal) to 1 part of hay. His carcass graded as good baby beef.

Steer No. 503 was a grade Hereford eleven months old. He was not full fed but was fed a good fair growing ration, the ratios of his feed being the same as for No. 505. His carcass graded as baby beef but a little thin and lacking finish. He was not as fat as No. 505.

The following steers belonged to the group known as "special maintenance." They were from the same sire and of the same herd of cattle, grade Herefords, and had run on grass until they were purchased for the experiment. They were then put on full feed until they were in prime condition. Their feed was 2.5 parts grain (8 corn to 1 linseed meal) to 1 part of hay. In February, 1908, steer No. 594 was killed as a check animal. The others were fed until September, 1908, when they were slaughtered.

Steer No. 594 showed shorthorn blood. He was a fat yearling (11 months) and he was in a nearly finished condition. His carcass was not as fat as No. 505 but fatter than No. 503. It graded as baby beef.

Steer No. 591 was on submaintenance from February to September, losing one-half pound a day. He was eighteen months old when killed. His carcass was very thin and graded as a "canner."

Steer No. 593 was on supermaintenance from February to September, gaining one-half pound a day. He was eighteen months old, and his carcass was in good condition grading as number two beef.

Steer No. 597 was on maintenance from February to September, neither gaining nor losing weight. He was eighteen months old, and his carcass graded as number three, being a little light for number two beef.

DISCUSSION OF DATA.

The results of the analyses are given in the following tables: Table I contains the moisture determinations in the adipose tissue, Table II the fat determinations, and Table III the protein determinations. The steers are arranged from left to right in the order of slaughtering and the fat samples in the order determined by the iodine values of steer No. 594.

TABLE I.—MOISTURE IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	10.044	4.484	5.263	8.676	5.481	19.700	7.497	4.842
Offal fat	16.620	9.517	12.410	14.642	10.957	38.876	17.969	12.631
Circulatory system	......	......	33.230	36.244	......	......	......	......
Loin fat	......	9.075	9.333	15.748	13.411	36.092	18.956	14.860
Head-tail fat	......	......	......	......	41.912	34.872	35.693	34.917
Inside chuck fat	25.055	11.213	9.814	21.140	14.414	47.324	20.737	15.503
Cod fat	......	17.920	11.782	12.675	13.035	45.490	13.920	12.541
Chuck-neck fat	......	......	......	......	23.289	49.349	29.459	19.592
Rib fat	......	10.677	10.913	23.294	14.273	40.465	21.859	19.434
Composite fat	......	......	......	......	20.047	42.366	25.492	19.989
Fat between hind legs	......	7.204	......	......	......	37.451	......	......
Flank fat	......	......	43.720	......	19.567	47.229	22.236	18.762
Rump fat	......	14.410	14.140	22.450	13.520	29.663	18.182	16.601
Round fat					20.754	44.868	26.640	20.927
Plate fat	......	......	see flank	......	22.991	24.946	24.899	21.134
Shin-shank fat	......	......	......	......	see head-tail	51.579	40.190	41.150
Outside rump fat	14.315	10.870	13.350	16.814	13.451	......	26.920	21.238
Outside rib fat	25.265	29.255	13.200	17.475	14.673	64.764	26.158	20.375
Same inner layer	......	......	6.957	......	......	......	......	......
Outside chuck fat	23.280	......	......	......	......	......	......	......
Brisket fat	......	......	......	......	......	56.221	27.651	25.568
Marrow fat	......	......	......	......	......	18.006	11.491	......

An inspection of these three tables shows that the percentages of moisture, fat, and protein are dependent upon the degree of fatness or condition of the animal. The fatty tissue of the thin animal in each and every case contains more protein and more moisture and less fat than does the fatty tissue of the fat animal. The order of increasing per cent. of fat and decreasing per cent. of moisture

TABLE II.—FAT IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	86.96	9.47	93.53	89.47	93.16	75.85	90.22	93.75
Offal fat	79.72	88.02	85.38	81.92	85.87	52.59	77.88	84.00
Circulatory system	.....	.....	59.06	54.91	.....	....	..	...
Loin fat	...	87.84	87.55	79.92	82.47	50.62	73.76	80.50
Head-tail fat	.....	....	.....	....	44.84	48.37	49.97	51.78
Inside chuck fat	68.80	86.84	88.21	73.80	81.56	36.46	71.74	79.28
Cod fat	.....	78.51	85.85	83.45	83.18	40.79	81.23	83.88
Chuck neck fat	...	.....	.....	....	70.25	31.77	58.72	71.85
Rib fat	.....	86.04	85.39	66.94	80.82	34.83	70.19	70.97
Composite fat	.....	.....	....	..	72.90	37.69	62.82	73.10
Fat between hind legs	.....	90.64	.....	..	.....	46.42	....	.....
Flank fat	.....	..	42.76	.....	72.58	25.05	68.20	72.73
Rump fat Round fat	....	{ 80.61	{ 80.64	} 70.13	82.36 71.01	59.15 39.64	74.18 63.61	78.28 69.09
Plate fat	.....	.....	see flank	....	69.75	66.63	66.17	66.52
Shin-shank fat	.....	....	....	....	see head-tail	25.64	44.31	40.47
Outside rump fat	80.63	86.56	83.64	78.37	83.48	....	62.05	40.47
Outside rib fat	66.30	64.72	83.66	76.94	81.69	8.27	67.23	73.91
Same-inner layer	.....	.....	91.67	.....	...	.....	....	.....
Outside chuck fat	69.55	....	.....	....	...	....	....	.....
Brisket fat	.....	.....	.....	....	....	25.80	65.40	68.66
Marrow fat	....	.....	.....	....	.....	79.57	87.30	.....

and protein is independent of age and is given in the following tabulation:

(1) Steer 591 very thin, graded as canner.
(2) Steer 503 fair condition, had never been fat.
(3) Steer 18 thin, graded as cutter.
(4) Steer 597 thin, graded as No. 3.
(5) Steer 594 rather fat baby beef.
(6) Steer 593 fairly fat No. 2 carcass.
(7) Steer 505 very fat baby beef.
(8) Steer 121 fairly fat No. 1 prime beef.

The packing houses grade their beef as follows: No. 1 is prime fat beef; No. 2 is a thinner carcass but very good; No. 3 is next in order; a cutter is poorer stuff than No. 3; and a canner is poorer than a cutter. Baby beef may vary in fatness either above or below No. 2, but it seldom is as fat as No. 1.

The internal fats contain less moisture and protein and more fat than do the skeletal samples and these again less moisture and protein and more fat than do the subdermal samples. In every case the kidney fat contains least moisture and protein and the offal fat ranks next. As an exception to this we may note that the inside chuck fat in the thinnest animals contains more moisture and protein than do some of the external samples. The marrow fat contains least protein, as is to be expected from the mealy consistency of marrow. The marrow fat of the thin animal 591 contains about 80 per cent. more moisture than does the marrow of the

TABLE III.—PROTEIN IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	2.63	1.13	1.48	2.13	1.66	4.78	1.88	1.15
Offal fat	3.23	1.71	2.13	3.26	2.73	7.30	3.03	2.70
Circulatory system	....	....	8.03	7.81	....	...	....	....
Loin fat	....	2.48	3.34	4.86	4.03	11.95	6.29	3.42
Head tail fat	....	....	....	....	12.46	10.74	9.99	9.91
Inside chuck fat	5.95	1.95	2.27	5.09	3.71	10.78	5.71	3.94
Cod fat	....	2.91	2.87	4.88	3.95	10.70	3.87	3.47
Chuck neck fat	...	....	.	....	6.73	14.13	8.66	5.27
Rib fat	....	2.83	4.02	9.26	5.25	16.43	7.04	8.01
Composite fat	....	....	....	...	7.76	13.84	9.21	6.95
Fat between hind legs	....	1.92	....	..	....	11.51	....	....
Flank fat	....	....	13.81	....	6.77	27.57	8.74	8.86
Rump fat Round fat	....	{ 3.86	{ 2.82	} 7.58	4.52 6.91	12.05 16.53	5.87 8.89	4.79 7.76
Plate fat	....	...	see flank	...	7.49	7.43	7.24	7.11
Shin shank fat	....	....	....	..	see head-tail	19.76	15.23	17.44
Outside rump fat	4.89	2.48	2.76	5.14	4.94	...	7.88	4.61
Outside rib fat	7.34	2.18	2.76	5.41	3.47	25.94	6.02	5.30
Same inner layer	...	..	1.54	...	....	.....	....	...
Outside chuck fat	6.48	....	....	....	...	.....	....	....
Brisket fat	....	....	....	..	....	14.53	5.83	5.80
Marrow fat	....	....	....	....	....	0.73	0.87	....

TABLE IV.—IODINE VALUES OF FATS.

	Steer No. 18. Thin, $3\frac{1}{2}$ yrs.	Steer No. 121. Fat, $3\frac{1}{2}$ yrs.	Geordie, very fat, 2 yrs.	Steer No. 505. Very fat, full fed, 11 mo.	Steer No. 503. Fair, not full fed, 11 mo.	Steer No. 594. Fat, 11 mo., check animal.	Steer No. 591. Very thin, 18 mo.	Steer No. 597. Thin, 18 mo.	Steer No. 593. Fairly fat, 18 mo.
Kidney fat	33.41	40.84	32.90	34.95	29.50	33.25	33.54	32.44	34.10
Offal fat	33.97	38.39	...	34.72	30.60	36.49	32.80	35.55	37.48
Circulatory system	...	...	...	31.78	31.17	...		...	...
Loin fat	...	43.64	...	39.50	32.30	41.85	38.30	39.12	41.31
Head-tail fat	...	...	...	...	...	...	35.35	41.04	42.38
Inside chuck fat	45.88	46.90	...	40.56	34.04	43.20	40.40	40.15	42.58
Cod fat	...	46.67	...	46.58	36.57	44.27	44.48	41.80	46.91
Chuck neck fat	...	...	...	...	...	44.75	39.93	42.44	45.05
Rib fat	...	45.18	...	44.61	36.32	45.02	36.58	42.25	47.14
Composite fat	...	...	...	...	...	45.90	36.74	42.59	45.54
Fat between hind legs	...	44.83	...	...	...	...	[illegible].51	...	...
Flank fat	...	...	...	45.32	...	46.23	43.68	44.16	47.36
Rump fat	...	46.32	...	44.05	37.13	47.55	39.55	40.70	42.89
Round fat						49.25	44.53	45.07	48.32
Plate fat	...		...	see flank	...	49.44	47.11	47.46	48.53
Shin shank fat	...	...	...	...	...	...	47.29	50.60	51.95
Outside rump fat	43.22	49.29	...	51.07	43.29	50.11	...	49.82	54.48
Outside rib fat	51.64	54.25	51.11	51.12	40.95	51.40	...	...	...
Same-inner layer	...	...	49.35	45.95	...	...	...	...	...
Outside chuck fat	46.68	...	...	...	...	...	...	...	...
Brisket fat	...	...	49.82	...	...	...	53.49	55.57	59.75
Marrow fat	...	...	...	...	...	...	58.93	53.92	...

fatter steer 597. The cod fat, on account of its situation in the scrotum and its being protected from the cold by the legs and body of the steer, acts more like an internal than like an external fat.

The physical and chemical constants of the rendered fats are given in Tables IV–VI. Table IV contains the iodine values, Table V the melting points, and Table VI the saponification values and the specific gravity of the fats of steer 594. The same order of steers and samples is adhered to.

By the study of Table IV it is clearly seen that the iodine values increase from inside to oustide while the melting points decrease in the same order. The cod fat again acts as inside fat. The order of increasing iodine values holds from inside to outside and is as follow: kidney, offal, circulatory, loin, head and tail, inside chuck, cod, chuck and neck, rib, composite, between hind legs, flank, rump, round, plate, shin and shank, outside rump, outside rib, marrow, and brisket. The values for the melting points (see Table V) do not decrease as uniformly, but they follow the same order in general. It appears that the rump fat might better take its position with the inside fats. This can be explained by the position of the cut. The rump lies on either side of the rectum near the tail. The high temperature maintained throughout the digestive tract extends to the end of the rectum. The fats closely surrounding this region would therefore be internal fats. The rump preponderates in this

TABLE V.—MELTING POINTS OF FATS.

	Steer No. 18.	Steer No. 121.	Geordie.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	47.40	45.05	46.30	46.30	47.88	48.10	47.00	48.10	47.30
Offal fat	48.58	45.20	...	45.30	48.15	47.10	47.50	47.30	46.30
Circulatory system	...	...	...	45.95	48.10	...	...	...	...
Loin fat	...	41.95	...	43.00	46.75	45.60	46.00	44.70	43.90
Head tail fat	...	...	...	...	...	...	45.00	45.20	43.50
Inside chuck fat	41.75	40.50	...	41.75	46.05	44.95	44.80	44.20	43.10
Cod fat	...	39.85	...	41.20	45.25	43.25	41.50	43.00	40.00
Chuck neck fat	...	...	...	...	...	43.80	44.70	43.00	41.50
Rib fat	...	40.30	...	39.80	46.55	43.10	46.10	43.60	41.00
Composite fat	...	...	...	...	...	43.60	44.70	44.30	42.00
Fat between hind legs	...	39.65	...	...	...	...	42.80	...	...
Flank fat	...	...	...	44.90	...	42.25	42.50	43.00	41.70
Rump fat	...	39.60	...	40.35	44.65	43.55	44.60	44.00	44.10
Round fat						41.30	42.40	41.70	41.30
Plate fat	...	...	...	see flank	...	42.40	42.70	42.00	40.70
Shin shank fat	...	...	...	...	...	...	40.70	39.40	38.50
Outside rump fat	41.65	35.25	...	36.60	42.60	39.90	...	38.70	35.70
Outside rib fat	38.38	35.55	33.20	36.90	44.60	40.70	...	38.30	34.80
Same-inner layer	...	...	35.35	38.70	...	...	...	...	...
Outside chuck fat	38.95	...	...	...	...	...	...	...	...
Brisket fat	...	...	33.85	...	...	...	35.50	35.10	32.10
Marrow fat	...	...	...	...	...	...	25.70	38.10	...

sort of fat. The position of the head and tail sample among the internal fats is explained by the head fats alone. A larger part of the fat composing this sample is taken from within the jaws and the cavities of the cranium, such as the orbital cavities, and from the region of the tongue. It is thus mostly internal fat. The shin and shank on the contrary is entirely external fat, the fat being taken from between the hide and the bones. The chuck and neck and the rib samples contain in the one case considerable fat located within a heavily muscled region and along the neck and thoracic cavity and in the other case fat lying near the digestive organs. So their position near the head of the carcass cuts is explained. The loin contains a large piece of kidney fat and it would thus be placed first of the carcass cuts. It will be seen that the youngest and thinnest animal has the lowest iodine values and highest melting points and that these vary as the increasing age and fatness of the animal, the very fat three and a half years old steer being highest in iodine values and lowest in melting points.

The saponification values for but six steers have been determined, and these show little relation to the location. A tendency may be noted showing that the saponification values decrease as do the melting points and go inversely to the iodine values. The values for specific gravity of one animal, given in Table VI, show but slight variations. There can be noted a tendency to follow the iodine values.

Table VII contains the iodine values of the fats in each sample, the steers being arbitrarily arranged in an order dependent upon their age and fatness. The order is as follows: *First*, steer 503, an eleven months old animal in fair condition but never at any time fat. Its age gave it the grade of baby beef. *Second*, steer 591, an eighteen months, very thin animal which had however been fat. It graded as low as a canner. Its having once been fat as well as its greater age place it above steer 503. *Third*, steer 597, thin, 18 months old, had been fat and graded as number 3; being fatter than 591 it would rank above it. *Fourth*, steer 18, a thin, three and a half years old animal grading as a cutter. Its greater age assisted by its having once been fat place it above 597. *Fifth* and *sixth*, steer 505 and steer 594. These two steers were 11 months old and both fat. Although steer 505 was judged to be the fatter of the two it is placed fifth in order. It is, however, difficult to decide between

TABLE VI.—SAPONIFICATION VALUES OF FATS.

	Steer No. 18.	Steer No. 121.	Geordie.	Steer No. 505	Steer No. 503.	Steer No. 594.	Specific gravity 100°/15° C. Steer No. 594.
Kidney fat	197.7	197.0	197.5	192.3	199.9	195.2	0.8604
Offal fat	198.8	195.8	.....	197.7	197.2	199.1	0.8568
Circulatory system	.....	.....	.....	201.7	196.1	.....	......
Loin fat	.....	193.3	.....	200.4	189.4	196.2	0.8582
Head-tail fat	.....	.....	.....	.....	.....	.....	......
Inside chuck fat	196.7	197.9	.....	199.3	197.5	195.5	0.8586
Cod fat	.....	199 5	.....	197.1	197.2	196.9	0 8589
Chuck-neck fat	.....	.....	.....	.....	.....	195.1	0.8602
Rib fat	.....	198.8	.....	200.4	185.2	197.9	0 8615
Composite fat	.....	....	.....	.....	.....	197.0	0.8592
Fat between hind legs	.....	201.1	.....	.....	.....	.....	......
Flank fat	.....	.....	.....	184.8	.....	194.0	0.8593
Rump fat	.....	194.30	.....	196.7	197.8	195.4	0.8591
Round fat						195.6	0.8606
Plate fat	.....	.....	.....	see flank	.....	196.0	0.8606
Shin-shank fat	.....	....	.....	.....	.....	.....	......
Outside rump fat	190.7	195.7	.....	196.0	183.1	196.6	0.8609
Outside rib fat	200 2	180.6	197.1	186.6	182.7	196.9	0.8605
Same-inner layer	.....	.....	202 3	199.2	.....	.....	......
Outside chuck fat	199 1	.....	.....	.....	....	.....	......
Brisket fat	.....	.....	206 1	.....	....	.....	......
Marrow fat	.....	.....	.....	.....	.....	.....	......

TABLE VII.—IODINE VALUES.

	Steer No. 503	Steer No. 591.	Steer No. 597.	Steer No. 18.	Steer No. 505.	Steer No. 594.	Steer No. 593.	Steer No. 121.
Marrow fat	.....	58.93	53.92	.....	.....	.....	.....	.....
Brisket fat	.....	53.49	55 57	.....	.....	.....	59.75	.....
Shin-shank fat	....	47.29	50.60	.....	.....	.....	51.95	.....
Outside rib fat	40.95	.....	.....	51.64	51.12	51.40	.....	54.25
Outside rump fat	43.29	.....	49.82	43.22	51.07	50.11	54.48	49.29
Plate fat	.....	47.11	47 46	.....	.....	49.44	48.53	.....
Round fat	.....	44.53	45.07	.....	....	49.25	48.32	.....
Cod fat	36.57	44.48	41 80	.....	46 58	44.27	46.91	46.67
Flank fat	.....	43.68	44.16	.....	.....	46.23	47.36	.....
Chuck-neck fat	.....	39.93	42.44	.....	.....	44.75	45.05	.. ..
Rump fat	.....	39.55	40.70	.....	.....	47.55	42.89	.. ..
Composite fat	.....	36.74	42.59	.....	.....	45.90	45.54	.....
Rib fat	36 32	36.58	42.25	.....	44 61	45.02	47.14	45.18
Inside chuck fat	34.04	40.40	40.15	45.88	40.56	43.20	42.58	46.90
Head-tail fat	.....	35.35	41 04	.....	.....	.....	42.38	.....
Loin fat	32.30	38.30	39 12	.....	39.50	41.85	41.31	43.64
Offal fat	30.60	32.80	35.55	33.97	34.72	36.49	37.48	38.39
Kidney fat	29.50	33.54	32.44	33.41	34.95	33.25	34.10	40.84
Circulatory system	31.17	...	....	....	31 78	.....	....	.....

the two. *Seventh*, steer 593, eighteen months old, and pretty fat, graded as number two beef. His age places him above the eleven months animals as well as does his fatness, and this places him above all the steers excepting steer 121. *Eighth*, steer 121, three and a half years old and fat. Steer Geordie was not included since but four of his fats were investigated. Investigation of the values demonstrates the validity of the above grading.

A source of considerable complication in the grading of the samples of fat from outside to inside including the carcass cuts is this: that in all but the special samples the fat composing the sample is taken from three separate and opposing regions. The carcass cuts contain fat which is purely subdermal, fat which is entirely internal, and fat which is intramuscular and between internal and external. As examples, note the chuck and the round. The chuck has subdermal fat and frequently large rolls over the shoulder. Then there is the fat lining the thoracic cavity and the inside of the neck. There is also beneath the scapulohumeral, or shoulder joint, a large pad of fat, which is probably a relic of its wild state and which was used to protect this joint and the muscles of the animal when jumping. The round has in addition to external fats a long ridge of fat running the greater part of the length of the femur. The loin has the external rolls of fats and the entirely different kidney fat. In order to remove these complications there are given in Table VIII the iodine values of the special samples only. The fat in any one sample is all of one kind. The steers are divided into two groups, the young steers (11 to 18 mo.) and the old steers (2 to 3½ years). This was done to avoid complications of age. The order for the young steers is as given just above. Geordie has been included among the old steers, and as he was but two years old though very fat he grades below the thin steer 18.

We may consequently state that the iodine values increase with both age and fatness. Since the relations between melting point and iodine value has been clearly demonstrated the melting point decreases with both age and fatness. As the animal increases in fatness the ratio of fat to water and protein increases. A fat animal placed upon a ration which is insufficient to support growth and maintenance will use his stored up fat for this purpose. He will take fat out of the fat cells and replace it with water. He will use up the lower melting point fats (olein) first and the fat that remains in the tissue will be of higher melting point (stearin). In confirmation of this, witness the increasing melting point and falling iodine value of the fat of the thin steer. The fatty tissue of the thin steer being soft and flabby is due to the great water content and not to a great olein content.

Table VIII.—Iodine Values of Special Samples.

	Steer No. 503.	Steer No. 591.	Steer No. 597.	Steer No. 505.	Steer No. 594.	Steer No. 593.	Steer Geordie.	Steer No. 18.	Steer No. 121.
Marrow fat	.....	58.93	53.92	.....	.....	.....	.....	.....	.....
Brisket fat	.....	53.49	55.57	.....	.....	59.75	49.82	.....	.....
Outside rump fat	43.29	.....	49.82	51.07	50.11	54.48	.....	43.22	49.29
Outside rib fat	40.95	.....	.....	51.12	51.40	.....	51.11	51.64	54.25
Same-inner layer	.....	.....	.....	45.95	.....	.....	49.35	.....	.....
Outside chuck fat	.....	.....	.....	.....	.....	.....	.....	46.68	.....
Cod fat	36.57	44.48	41.80	46.58	44.27	46.91	.....	.....	46.67
Fat between hind legs	.....	41.51	.....	.....	.....	.....	.....	.....	44.83
Inside chuck fat	34.04	40.40	40.15	40.56	43.20	42.58	.....	45.88	46.90
Offal fat	30.60	32.80	35.55	34.72	36.49	37.48	.....	33.97	38.39
Kidney fat	29.50	33 54	32.44	34.95	33.25	34.10	32.90	33.41	40.84
Circulatory system	31.17	.....	.....	31.78	.....	.....	.....	.....	.....

CONCLUSIONS.

In the fatty tissue of animals the amounts of fat and of moisture and protein are intimately connected, a high per cent. of fat being accompanied by a low per cent. of moisture and protein.

In the fatty tissue the per cent. of fat increases with the fatness of the animal while the moisture increases with the leanness. This is dependent upon condition irrespective of age.

The per cent. of fat in the fatty tissue of animals is dependent upon the location in the animal body. The per cent. of fat increases from outside to inside while the per cent. of moisture increases from inside to outside.

The iodine value of fat from the fatty tissue of an animal increases with the age of the animal while the melting point decreases.

The iodine value of fat from the fatty tissue of an animal increases with the fatness of the animal while the melting point decreases.

The iodine value of fat from the fatty tissue of animals increases from inside to outside of the animal body while the melting point decreases.

The iodine value and melting point are closely related, the one rising as the other falls.

The specific gravity seems to follow the iodine value while the saponification value varies as the melting point.

Credit is here given Mr. J. O. Halverson for the determination of part of the iodine and saponification values and melting points.

Columbia, Missouri,
June, 1909.

[Contribution from the Chemical Laboratory of the New York Agricultural Experiment Station.]

A VOLUMETRIC METHOD FOR THE DETERMINATION OF CASEIN IN MILK.[1]

By Lucius L. Van Slyke and Alfred W. Bosworth.

In 1892 there was worked out in the chemical laboratory of this station a method for the determination of casein in cow's milk.[2] This method, after careful trial by the Association of Official Agricultural chemists, was adopted as "official."[3] It was realized that the method was adapted only for use in well-equipped laboratories and in the hands of trained chemists. Unsuccessful efforts were made at different times to devise a simple, direct volumetric method, requiring less apparatus, time, manipulation and skill. Several attempts have been made by others to find such a method, among which we mention the following: (1) Estimation of casein, a preliminary study.[4] (2) Quantitative estimation of casein.[5] (3) A new method for the determination of casein.[6] These and other proposed methods are open to several practical objections.

In making a study of the accuracy of the results given by the method of Matthaiopoulos, it was found that a reconstruction of its details could easily be utilized in devising a method of equal accuracy but of much greater simplicity and rapidity.

The method which has been thus worked out is, in brief, as follows: A given amount of milk, diluted with water, is made neutral to phenolphthalein by addition of a solution of sodium hydroxid. The casein is then completely precipitated by addition of standardized acetic acid; the volume of the mixture is made up to 200 cc. by addition of water and then filtered. Into 100 cc. of the filtrate a standardized solution of sodium hydroxid is run until neutral to phenolphthalein. From the difference between the amount of acid and the amount of alkali used, a simple calculation enables one to determine the percentage of casein in the milk examined.

This method is based upon the following well-known facts: (1) Uncombined casein is insoluble in milk-serum, or water, or very dilute acids.[1] (2) It is acid in properties and combines with alkalis to form definite chemical compounds, which are neutral to phenolphthalein.

Of the total amount of acid used in the process of precipitating casein, a portion is taken to set casein free from combination, thus forming a soluble neutral salt and an insoluble compound (free casein) possessing the properties of an acid; and, on filtration, this amount of acid, as free casein, is removed from the mixture. The balance of the acid used in the process is accounted for in the filtrate on titration with alkali. Therefore, the difference between the total amount of acid used and that accounted for in the filtrate by titration with alkali represents the amount of acid corresponding to the casein present in the milk examined.

Since one gram of free casein neutralizes 8.8378 cc. of tenth-normal sodium hydroxide (or 1 cc. of tenth-normal sodium hydroxide equals 0.11315 gram of casein),[2] we have a definite basis for estimating the amount of casein in any given case, when we know the amount of alkali it neutralizes.

DESCRIPTION OF METHOD.

(1) *Measuring and Diluting Sample of Milk.*

The milk to be examined is well mixed and 20 cc. run into a 200 cc. flask, to which is added about 80 cc. of water.

(2) *Neutralizing the Milk.*

Add 1 cc. of phenolphthalein solution to the diluted milk and then run into it a solution of a sodium hydroxid until a faintly, but distinctly, pinkish shade of color remains through the mixture even after considerable agitation. Any marked excess of alkali should be avoided.

(*a*) *Preparation of a Color-standard.*—More uniform and satisfactory results can be obtained in this step of the process by preparing a color-standard for comparison. Our method of accomplishing this is as follows: about 20 cc. of

[1] Presented in abstract at the meeting of the American Chemical Society, Detroit, June, 1909.

[2] *J. Am. Chem. Soc.*, **15**, 635.

[3] *Bull.* **15**, *U. S. Dept. of Agr., Div. of Chem.*

[4] V. H. Arny and T. M. Pratt, *Am. J. Pharm.*, **78**, 121.

[5] T. B. Robertson, *J. Biol. Chem.*, **2**, 328.

[6] G. T. Matthaiopoulos, *Z. anal. Chem.*, **47**, 492.

[1] L. L. Van Slyke and D. D. Van Slyke, *Am. Chem. J.*, **38**, 409.

[2] *Z. anal. Chem.*, **47**, 495.

fresh skim-milk and 80 cc. of water are put into a 200 cc. flask and a small amount of mercuric chlorid added. A few drops of ordinary carmine ink are considerably diluted with water and this is carefully added, a few drops at a time, to the diluted skim-milk until a faint but distinct pinkish coloration appears. This can be more readily and accurately perceived by placing beside the flask another flask half full of uncolored, diluted skim-milk. The coloration must be as slight as possible and yet be appreciably distinct when compared with uncolored milk. After the color-standard has been prepared, the flask is stoppered and kept in a dark place when not in use. With some carmine colors, the pinkish shade in the milk may deepen on standing, especially when exposed to light. If at any time this is observed, the proper shade can be reproduced by slight dilution with skim-milk. The object of using skim-milk in preparing a color-standard is to avoid the presence of fat, which, in case of whole milk, separates on standing, adheres to the sides of the flask and obscures the color.

(*b*) *Use of Color-standard.*—In neutralizing a sample of milk, the color-standard is placed beside the sample under examination for constant comparison after each addition of alkali. The flasks should be placed on a white surface and in a good light in order to render more sharp the observation of the coloration. In fresh milks, it is usually found that 3 or 4 cc. of tenth-normal alkali are sufficient to neutralize the milk. In cases where milk is not strictly fresh or where it has been kept for some time with mercuric chlorid, usually from 5 to 10 cc. may be required. After the milk begins to show signs of neutrality, the alkali is added a drop at a time, the flask being shaken and the color being observed after each addition.

(3) *Precipitation of Casein.*

(*a*) *Addition of Acid.*—Into the neutralized sample of diluted milk, which should be at a temperature of 18° C. to 24° C., one now runs tenth-normal acetic acid, adding the acid approximately in 5 cc. portions and agitating vigorously for a few seconds after each addition. It is usually safe to add about 25 cc. of acid before examining the milk to see if the casein is separating in the form of white flakes. After adding 25 cc. and shaking, the mixture is allowed to come to rest. If enough acid has been added, the casein separates promptly in large, white flakes, and, on standing a short time, the liquid above the settled casein appears clear and not at all milky. If the addition of 25 cc. of acid is insufficient to separate the casein properly, add 1 cc. more of acid and shake; continue the addition of acid, 1 cc. at a time, until the casein is observed to separate promptly and completely on standing at rest a short time. The number of cc. of acid used to affect precipitation is noted and this result is recorded as A.

(*b*) *Influence of Temperature.*—For convenience and uniformity of results, the temperature of the mixture at the time of the addition of acid may be between 18° and 24° C. Under these conditions, we have found that in most of the milks with which we have worked, 30 cc. of tenth-normal acetic acid gives satisfactory results. In some cases, especially with the milk of cows far along in lactation and high in casein (3.5 to 4 per cent.), we have had to use as high as 35 to 40 cc. of acid. We have seldom found any case in which 25 cc. of acid was excessive. The amount of acid may be 2 or 3 cc. in excess of that required to effect complete precipitation without seriously affecting the accuracy of the results, provided the temperature of the mixture is below 24°. At higher temperatures, good results are attainable, but care must be exercised not to use much excess of acid; and, of course, the higher the temperature, the less will be the amount of acid required for precipitation. Extra care must be used at higher temperatures in regard to the use of any marked excess of acid for the following reason: The higher the temperature, the more easily does casein dissolve in the presence of free acid,[1] the effect being to reduce the results of the determination in percentage of casein. In working at temperatures under 18°, the casein separates more slowly or requires more acid to separate promptly. In case of milk that is much below 18°, it is well to use for dilution water that is at a temperature of about 27°.

(4) *Filtration of Casein.*

After the casein is completely precipitated, water is added to the mixture up to the 200 cc. mark and the contents are vigorously shaken for 10 or 15 seconds, in order to make the distribution of acid through the mixture as uniform as possible. The contents of the flask are then poured upon a dry filter. It is well generally to allow the filtration to continue until practically all of the liquid has been filtered.

[1] *Am. Chem. J.*, **38**, 409.

(*a*) *Rapidity of Filtration.*—The usual time of filtration should not exceed 3 to 5 minutes, when precipitation is complete. The rapidity depends upon the temperature of precipitation and the completeness of the separation of casein. In general, the higher the temperature of the mixture when precipitated with acid, the more rapid should be the filtration, other conditions being uniform. In case of insufficient acid, the filtration is slower.

(*b*) *Appearance of Filtrate.*—The filtrate should be quite clear, though this is not always a sure indication that the right amount of acid has been added to effect complete precipitation and release casein entirely from its combination. Sometimes the filtrate may be clear when not quite enough acid has been added, in which case the percentage of casein found is apt to be low; under such circumstances, filtration is usually slow. In case of milk rich in fat, a slight turbidity may appear, due to fat-globules in the filtrate. The filtrate should be free from all signs of marked turbidity or anything like milkiness. If such a filtrate appears, a new sample of milk should be taken and the operation repeated from the beginning, more acid being used than before.

(5) *Titration with Alkali.*

After filtration is completed, one takes 100 cc. of the filtrate and runs into it tenth-normal solution of sodium hydroxide until the reaction is neutral to phenolphthalein. The number of cubic centimeters of alkali used is noted and this result is recorded as B. The exact neutral point is not perfectly sharp on account of the presence of phosphates, and the appearance of the end-reaction is not as pronounced as might be desired. However, with experience one should have no difficulty in getting within one drop of the correct amount of alkali. One should work to obtain the same shade and duration of color every time. In general, one takes for the end-reaction the appearance of a faint but distinct pink coloration, which remains clearly marked through the solution for half a minute or longer before beginning to fade. In the case of milks rich in phosphates, the solution usually grows quite turbid as the neutral point is approached, making it more necessary to use caution in observing the color of the end-point of the reaction.

If one desires to make a second titration of the same filtrate, one can use 50 cc. of the remaining portion, multiplying the result by 2 and recording this as B.

(6) *Calculation of Results.*

The calculation of the percentage of casein from (*a*) the amount of acid used (A) in precipitating the casein and (*b*) the amount of alkali used (B) in neutralizing 100 cc. of filtrate, is very simple. Divide A by 2, from the result subtract B and multiply the result by 1.0964; or expressed as a formula,

$$(A/2 - B) \times 1.0964 = \text{Per cent. of casein.}$$

By using 22 cc. of milk instead of 20 cc., the multiplication by the factor can be obviated, the formula then becoming simply $A/2 - B$, each cc. of tenth-normal solution being equivalent to 1 per cent. of casein.

(7) *Use of Preservatives.*

In making casein determinations by this method, it is desirable when possible to use milk comparatively fresh. Milk that is sufficiently acid to coagulate on boiling or that is well soured can not be used with satisfactory results. However, by adding to fresh milk powdered mercuric chloride in the approximate proportion of 1:1000 or 1500, and then keeping the mixture in a cool place, we have been able to obtain satisfactory results with milk that had been kept for two to three weeks. Milk thus treated should be shaken often enough to keep the fat well incorporated in the body of the milk.

RESULTS ILLUSTRATING USE OF METHOD.

The data below represent the results obtained by three different workers in comparison with the "official" method. The samples of milk used were obtained from individual cows. It will be observed that results usually come within 0.2 per cent. of those obtained by the official method.

PERCENTAGES OF CASEIN IN MILKS AS DETERMINED BY DIFFERENT WORKERS.

No. of sample.	Official method.	Volumetric method. 1.	2.	3.
1	3.09	3.00	2.95	3.10
2	3.36	3.40	3.45	3.45
3	3.21	3.30	3.40	3.30
4	3.16	3.20	3.20	3.10
5	2.95	2.90	2.90	2.80
6	3.11	3.05	3.10	3.15
7	2.66	3.00	3.00	3.05
8	3.34	3.20	3.00	3.10
9	3.62	3.55	3.60	3.55
10	3.20	3.30	3.20	3.10
11	3.22	3.20	3.00	3.10
12	2.68	2.85	2.75	2.80
13	2.92	3.00	2.90	2.90
14	2.79	2.85	2.80	2.95
15	2.84	2.85	2.80	2.70

It may be stated in this connection that the use of other acids (hydrochloric and sulphuric) and of

other alkalis (hydroxides of barium and calcium) was applied to the method but did not give satisfactory results. In the Matthaiopoulos method, sulphuric acid is used. The especial advantage of dilute acetic acid, as compared with the other acids tried, lies in its smaller dissolving and adsorbing properties for casein.[1]

By this method the percentage of casein can be determined in a sample of milk in 12 to 15 minutes, when one has at hand the solutions and apparatus needed. With proper conveniences a dozen determinations can be made in 45 to 60 minutes after one has acquired acquaintance with the operations of the method.

ON THE RELATION OF NATIVE LEGUMES TO THE SOIL NITROGEN OF NEBRASKA PRAIRIES.

By F. J. Alway and R. M. Pinckney.

Received August 4, 1909.

In a recent botanical study[2] Warren has called attention to the entire absence of published data on the relation between the native legumes and the amount of nitrogen in virgin prairie soils. He expresses the opinion that the amount of combined nitrogen added by rain and snow together with the amount of free nitrogen fixed by non-symbiotic bacteria "do not furnish a satisfactory explanation of the presence of such large quantities of nitrogen in the soil." His conclusions are based upon counts, made in 1908, of the leguminous plants on measured plots in prairie fields in different parts of Nebraska and adjoining states.

In the course of an investigation, the results of which are not yet published, we had in the preceding summer and autumn made a chemical study of the same question in the case of one of the prairie fields mentioned by Warren, from whom we have learned that his count was made on an adjoining but slightly lower portion of the gently sloping field. What data we have on the native leguminous plants, together with some of that on the soil, have been assembled for the present article. The removal of the junior author to the Montana Agricultural Experiment Station, a year ago, interrupted the continuation of the study.

The prairie referred to is in University Place, a suburb of Lincoln, and since 1889 has formed a part of the campus of the Nebraska Wesleyan University. Since that time the portion of it studied by both Warren and ourselves has been mown annually for hay; during the rest of the year it has been little visited except by children in search of wild flowers. Previous to 1889 it had formed part of a large pasture. This part of the field is typical of the virgin upland prairie of eastern Nebraska, as indicated by Warren's data obtained on July 2, 1908.

On July 12 and 13, 1907, we measured off a plot 50 ft. by 50 ft. and from this gathered all the leguminous plants, cutting them at the surface of the ground. The plants were exposed on the shelves of a storeroom until they were air-dry, and then weighed, ground and analyzed. From what we considered a representative square yard on this plot the non-leguminous plants were similarly gathered, dried, weighed and analyzed. We are indebted to Dr. F. D. Heald, both for assistance in the search for legumes and for the identification of the species. Soon after the plants had been gathered the prairie was mown for hay. There was so little aftergrowth of either legumes or grasses that it was not considered worth while to make a second collection. The growth of vegetation in 1907 may safely be considered representative of an average year.

Table I.

Legumes.	Yield of air-dry matter. On plot 50 ft. × 50 ft. Grams.	Yield of air-dry matter. On 1 acre. Pounds.	N in air-dry matter. Per cent.	Wt of N per acre. Pounds.
1. Amorpha canescens	6,692	256.8	2.23	5.73
2. Kuhnistera candida	2,700	103 6	1 85	1.92
3. Astragalus crassicarpus	890	34.2	2.41	0.82
4. Psoralea argophylla	154	5.9	1.50	0.09
Non-leguminous plants	65,278	2,505.3	1.13	28.31
Total	75,714	2,905.8	....	36.87

The aerial portion of the leguminous plants collected contained 8.56 lbs. of nitrogen per acre. The aftergrowth of legumes and the leguminous plants which may have died and disappeared before the date of collection might increase the total annual production of nitrogen in the aerial parts to 10 lbs. per acre. It is not known what portion of the total nitrogen contained in leguminous plants is that which has been fixed by the symbiotic bacteria, and accordingly, we cannot estimate how much of the 10 lbs. per acre has been derived from the nitrogen compounds in the soil. What little data we have on the growth of alfalfa on Nebraska soils indicate that the nitrogen contained in the roots is about equal to that derived from the soil

[1] *Am. Chem. J.*, **38**, 409.

[2] "Notes on the Number and Distribution of Native Legumes in Nebraska and Kansas," *Circular* **31**, *Bur. of Plant Ind., U. S. D. A.* (June, 1909).

by the entire plant. If this holds true for the native legumes the amount of nitrogen fixed by the symbiotic bacteria would be about twice the amount added to the soil by rain and snow. Assuming that the non-symbiotic bacteria are able to fix one-half pound of nitrogen for every 100 lbs. of carbohydrate consumed, the carbohydrates contained in the non-leguminous plants, amounting to about 1600 lbs., would enable them to fix about 8 lbs. per acre each year. Thus the amounts of nitrogen added to the soil by the three agencies, *viz.*, the precipitation, the bacteria associated with legumes and the non-symbiotic bacteria, would bear approximately the ratio 1 : 2 : 2, provided that the whole of the aerial portion of the legumes was incorporated with the soil and that the whole of the carbohydrates of the aerial portion of the non-leguminous plants was oxidized by non-symbiotic nitrogen-fixing bacteria. Considering the incompleteness of any such disposition of the aerial portions of prairie vegetation it seems probable that the amounts of nitrogen added by the three agencies mentioned above are more nearly equal than is indicated by the above ratio.

TABLE II.—DISTRIBUTION OF NITROGEN IN SOILS OF NEBRASKA PRAIRIES

Field. Nearest town, approximate longitude.	A.	B Lincoln, 96° 40′.	C.	D.	E. Elgin, 98° 7′.	F. Hastings, 98° 50′.	G. Imperial, 101° 40′.	H.	I. Madrid, 101° 35′.
First inch	0.346	0.465	0.416	..	0.296	0.276	0.162	0.084	0.186
Second inch	0.315	0.312	0.344	...	0.263	0.226	0.128	0.078	0.135
Third inch	0.279	0.265	0.271		0.227	0.191	0.140	0.088	0.134
Fourth inch	0.262	0.234	0.230	.	0.205	0.178	0.149	0.079	0.134
Fifth inch	0.247	0.230	0.209	..	0.195	0.165	0.104	0.071	0.125
Sixth inch	0.234	0.214	0.198	...	0.192	0.159	...	0.067	0.110
Seventh inch	0.215	0.197	0.196	.	0.177	0.153	.	0.062	0.102
Eighth inch	0.201	0.190	0.190	...	0.169	0.145	...	0.060	0.096
Ninth inch	0.189	0.184	0.173	...	0.155	0.149	...	0.054	0.092
Tenth inch	0.181	0.177	0.165	...	0.149	0.143	..	0.053	0.102
Eleventh inch	0.176	0.165	0.158	...	0.133	0.141	.	0.057	0.086
Twelfth inch	0.173	0.165	0.153	..	0.128	0.138	....	0.065	0.089
First foot	0.240	....		0.265	0.201	0.170	0.127	0.068	0.117
Second foot	0.111	....	....	0.190	0.098	0.091	....	0.043	0.077
Third foot	0.063	....	...	0.118	0.055	0.052	....	0.035	0.038
Fourth foot	0.045	...		0.061	0.052	0.041	....	0.027	0.019
Fifth foot	0.042	...		0.074	0.058	0.035	...	0.025	....
Sixth foot	0.042	..		0.061	0.053	0.029	..	0.023	..

The nitrogen content of the soil of the above described prairie is shown in the table above—Field A. Thirty-five samples to a depth of six inches were taken from different places in the field. The nitrogen content ranged from 0.250–0.317 per cent., with an average of 0.284 per cent. Fields B, E and F, also, are representative of the upland loess soils[1] of Eastern Nebraska. Fields G and H are representative of the heavier and lighter types, respectively, of tillable soil on the high plains of western Nebraska. Fields C and D are typical of the lowland loess soils[1] of eastern Nebraska which owe their depth of black soil to the deposit by summer floods of the surface soil eroded from the higher lands. The average of 29 samples from such deposits collected after a flood in 1908 showed 0.230 per cent. nitrogen. Field I is typical of an unusual accumulation of organic matter in western Nebraska, the wind playing the same part there that the water does in the eastern part of the state. The accumulation, however, had taken place on the lee side of a low ridge instead of in a valley. The common idea as to the great depth to which black soil extends on these prairies is erroneous and is due, largely, to exposures of such unusual accumulations of organic residues.

The upland prairies of eastern Nebraska contain in the first two feet of soil about 10,000 lbs. of nitrogen per acre. This amount is so small that its accumulation may be accounted for by any one of the three agencies mentioned, a fixation of nearly 100 lbs. of nitrogen per acre per annum having been observed at Rothamsted in the case of a piece of land "which for the last twenty-five years has been allowed to run wild and assume a natural prairie condition of self-sown weeds and grasses that are never taken away but left to rot where they die down."[2]

Evidently the nitrogen content of the upland prairie soils has long since reached equilibrium and an accumulation of nitrogen is to be expected only where the original amount has been reduced by erosion or by cultivation.

LABORATORY OF AGRICULTURAL CHEMISTRY,
UNIVERSITY OF NEBRASKA,
LINCOLN, NEBRASKA.

[1] *Marshall silt loam* according to the nomenclature of the Bureau of Soils, U. S. Dept. of Agr.

[1] *Wabash silt loam* according to Bureau of Soils, U. S. Dept. of Agr.

[2] A. D. Hall, Cantor Lectures on Artificial Fertilizers, p. 14 (1907).

SUGGESTED STANDARDS FOR MAPLE SUGAR AND SYRUP.

By H. W. Cowles, Jr.

Received August 14, 1909.

Maple sap, while being concentrated to a syrup, throws out a certain sediment, called "nitre," composed largely of salts of calcium, insoluble in water. When this "nitre" is removed by filtration or sedimentation the resulting syrup will always have an ash above 0.45 per cent., usually above 0.50 per cent. When this clarified syrup is further concentrated to a sugar, it will have an ash of about 0.65 per cent. on the water-free basis and thus conforms to the U. S. Standards. When this sugar is dissolved in the requisite amount of water it will again yield a syrup with 0.45 per cent. ash. Now, if the original maple sap is concentrated to a sugar without the removal of the "nitre," the sugar will have an ash well above the standard of 0.65 per cent. and, on solution in the requisite amount of water and filtration to remove insoluble matter, will yield a syrup which has an ash above 0.45 per cent. This insoluble matter or "nitre" gives an ash which is just as much "maple" as the mineral matter which is in solution in the syrup.

During the season just past, several samples of maple sugar were examined from one locality of a large maple-producing section from which, although they conformed to the U. S. Stds., it was impossible to make legal syrups. The average ash was 0.79 per cent., well above the limit prescribed in the standards, but syrup made from the samples had an average ash of 0.42 per cent.—below the standard. It was suspected that some one had taken advantage of the fact that, although 0.65 per cent. maple sugar ash is necessary for a legal sugar, it is not necessary, in order to comply with the standards, that all this ash-giving matter shall go into the syrup made from the sugar. It is therefore possible to take a maple sugar containing a large quantity of this "nitre," and a correspondingly high ash, and add cane sugar to it in such proportion that the resulting sugar will still have an ash above the limit of 0.65 per cent. As the standards are now placed the sugar is legal if it contains 0.65 per cent. maple sugar ash on the water-free substance. But owing to the large amount of "nitre" this sugar will not yield a legal syrup on solution in water and filtration.

A careful analysis of the ash for water-soluble and insoluble portions and the alkalinity of each may show that cane sugar has been added to a maple sugar containing a large amount of "nitre," but a simpler method and one which conforms to actual practice is the placing of the ash of a maple sugar on a syrup basis instead of a water-free basis as at present. There can be no objection to leaving a proper lower limit on the ash determined as it exists in the sugar and expressing it on a water-free basis for uniformity, but the result desired, the stopping of adulteration, is not prevented. It simply shows how low in ash a maple sugar may be and still be pure. The ordinary maple sugar of commerce has not been clarified beyond the possible skimming off of impurities that come to the surface during concentration; accordingly all the "nitre" or salts rendered insoluble by boiling and concentrating remain in the mixture and are sold as sugar. When a syrup is made from this sugar, this insoluble portion has to be removed in order to produce a clear merchantable article. If the syrup is put up for consumption direct from the sap without going through the sugar stage, this insoluble matter, or "nitre" is removed, although occasionally it is found in the bottom of cans of syrup which have been carelessly prepared.

From the above it is easily seen that the ash of a commercial sugar may be much higher than if made from a filtered syrup, and, conversely, the ash of a filtered syrup made from a commercial sugar will be much lower than that of the sugar when both are calculated on the water-free basis. The amount of insoluble matter present in a sugar, which must be removed to make a clear syrup, varies with the condition of the sap and the method of preparation, long-continued boiling being a chief factor. Whatever the amount, the larger part of it consists of lime salts, which show up as total ash in the analysis. Therefore, as above stated, the careful analysis of the ash of many pure sugars would tend to establish standards which would to a certain extent check adulteration; but the limits would necessarily be wide and a simpler method is as follows: To 50 grams of the sugar in a small glass stoppered flask add 26 cc. (25 grams) of boiling water. Dissolve by shaking thoroughly. Filter, while still warm, through ordinary filter paper into a small narrow-necked flask, keeping the funnel covered with a watch glass to prevent undue loss by evaporation. Determine the specific gravity of the syrup thus made at standard temperature and from this calculate the amount of total solids as sugar by reference to tables, the balance being water. De-

termine the ash and calculate to a uniform basis of water content, for instance the U. S. Std. of 32 per cent. This is necessary because of the varying amount of moisture present in the original

Description.	Moisture.	Ash. Total.	Ash. Water-soluble.	Ash. Water-in-soluble.	Alkalinity, cc. N/10 acid per 100 grams sample. Water phenol-phthalein.	Alkalinity. Soluble methyl orange.	Alkalinity. Water-in-soluble methyl orange.	Total.	Ash, dry basis.	Ash, syrup basis (32% water).
New York maple sugar (pure)	2.70	1.116	0.392	0.724	29.0	53.0	128.0	181.0	1.147	0.800
New York sugar syrup (filtered) 50 gm. sugar, 25 gm. water	41.28	0.455	0.311	0.144	16.0	38.0	41.0	79.0	0.775	0.527
New York sugar—60 parts Cane sugar—40 parts	1.5	0.723	0.302	0.421	17.5	31.0	75.0	106.0	0.779	0.499
Syrup of above (filtered) Mixed sugar—50 gm., Water—25 gm.	34.8	0.322	0.184	0.138	7.0	15.5	31.0	46.5	0.494	0.336
Canadian maple sugar (pure)	6.1	0.861	0.853	0.476	36.0	....	88.0	....	0.917	0.624
Canadian sugar syrup (filtered) 50 gm. sugar, 25 gm. water	39.44	0.476	0.301	0.175	18.0	35.0	40.0	75.0	0.786	0.554
Canadian sugar—75 parts Cane sugar—25 parts	2.0	0.643	0.302	0.341	29.0	40.0	61.0	101.0	0.656	0.450
Syrup of above (filtered) Mixed sugar—50 gm., Water—25 gm.	35.3	0.373	0.206	0.167	12.5	26.0	39.0	65.0	0.576	0.382

50 grams of commercial sugar. The per cent. of moisture can be calculated roughly from the amount of water present in the weak syrup in excess of $33^1/_3$ per cent. which would result from the solution of 50 grams anhydrous sugar in 25 grams water. If no cane sugar has been added the total ash will be over 0.45 per cent., usually 0.50 per cent. If cane sugar has been added, the amount can be determined approximately, by calculation with 0.45 per cent. as a basis.

The analyses of two sugars of known purity are given in the following table, together with the syrups made from them as above outlined. The same table contains comparable results on mixed sugars made from each by the addition of the stated amounts of cane sugar.

It will be seen that both mixed sugars would have to be passed as pure under the present standards. The other methods commonly in use for the detection of adulterated maple products depend for their accuracy on the same substances as does the ash, hence are unreliable in detecting this particular condition.

In the following table are given the results on fourteen samples of commercial maple sugars, analyzed by the above method.

The samples were carefully taken by boring with a long auger through the center of tubs holding about 60 lbs. sugar each, and then mixing thoroughly the sugar brought up by the auger. A syrup made commercially from these tubs would not have an ash much above 0.40 per cent. and the analyses show the reason. Before giving suggestions as to the wording of the standard which it is believed would prevent sophistication of maple sugar, a word should be said about the water content of maple syrup.

Sample No.	Solids	Moisture	Ash on original sugar.	Ash on dry basis (0.65% std.).	Alkalinity to phenolphthalein, 100 g. sugar.	Alkalinity to methyl orange, 100 g. sugar.	Ash of syrup—50 g. sugar, 25 g. water.	0.45% ash on syrup containing 32% water.
1	89.95	10.05	0.59	0.655	20.0	103.0	0.31	0.35
2	83.0	17.0	0.77	0.93	33.0	134.0	0.46	0.56
3	87.4	12.6	0.70	0.80	29.0	116.0	0.42	0.48
4	89.1	10.9	0.80	0.90	32.0	153.0	0.39	0.44
5	87.57	12.43	0.45	0.51	8.0	43.0	0.16	0.18
6	87.9	12.1	0.83	0.94	32.0	154.0	0.43	0.49
7	88.3	11.7	0.66	0.75	26.0	123.0	0.36	0.42
8	87.5	12.5	0.68	0.78	30.0	113.0	0.44	0.51
9	87.6	12.4	0.81	0.92	29.0	143.0	0.38	0.44
10	89.0	11.0	0.66	0.74	18.0	118.0	0.31	0.36
11	90.4	9.6	0.81	0.90	32.0	145.0	0.36	0.40
12	88.2	11.8	0.72	0.82	34.0	145.0	0.37	0.43
13	91.3	8.7	0.76	0.83	31.0	147.0	0.40	0.44
14	91.0	9.0	0.25	0.27	8.0	49.0	0.12	0.13

The present U. S. Standard for syrup requires at least 0.45 per cent. maple ash and not more than 32 per cent. of water. Starting with a "pure" maple sugar containing just 0.65 per cent. maple ash on the water-free basis, which would be legal, it will readily be seen that even if all the ash-giving substances go into solution, a syrup made therefrom can only contain 30.75 per cent. moisture in order to have 0.45 per cent. ash. Such a syrup would be heavy and unpalatable and when exposed to the air for even a short time would readily crystallize. The ash of a syrup from any sap measures quite accurately the amount of solids-not-

sugar present and consequently the ability of the syrup to resist crystallization with a low water content. This fact was recognized by the Standards Committee when it made 30 per cent. the maximum water limit for cane syrup and molasses with 2.5 per cent. ash, as against 35 per cent. of water for a sugar syrup with no ash or solids-not-sugar. One-half per cent. ash represents approximately the solids-not-sugar that will permit the lowering of the water limit by 1 per cent. If the same reasoning were applied to maple syrups with an ash content of about ½ per cent., which all concede to be correct, the water limit would be placed at 34 per cent. This theory is borne out by practice. The maple syrups now on the market have an average water content of from 31½ to 32½ per cent., a fear of resulting crystallization keeping the manufacturers from going below this limit. This is too close to the legal limit to be comfortable. A slight variation in testing the degree in boiling down might make an otherwise pure syrup illegal. If the standard were raised to 34 per cent. a limit would be established that would be practical not because it enables the manufacturer to add 2 per cent. of water to his product but because it places a limit that would not have to be approached so dangerously near in order that a merchantable product may be obtained. The manufacturer would keep his syrup between 32 and 33 per cent. of water because fermentation and crystallization make very good watch-dogs to keep him from varying either way to any extent.

If the standard for the water content of syrup were 34, the ash of sugar on a water-free basis would have to be made 0.68 per cent. to correspond. The ash of the sugar may be higher than this, but at least 0.68 per cent. on a water-free basis must go into solution in water in order that a legal syrup may be made from it.

As standards, therefore, the following are suggested:

Maple sugar is the solid product resulting from the evaporation of maple sap or maple syrup and contains not less than 0.68 per cent. of maple sugar ash in the water-free substance, and on solution in water will yield a clarified maple syrup, containing not less than 0.45 per cent. maple syrup ash.

Maple syrup is the product resulting from the evaporation of maple sap or the solution of maple concrete or sugar and contains not less than 0.45 per cent. maple syrup ash and not more than 34 per cent. water.

ADDRESSES.

THE NEED OF METHODS OF ANALYSIS OF PHARMACOPOEIAL ARTICLES.[1]

By B. L. Murray.

The United States Pharmacopoeia is well and intimately known to all the pharmaceutical chemists here to-day. It is probably known in a general way to all the chemists of our association. But, notwithstanding this, the book is such an important one that it is worthy our close attention, for a short time at least. It is, without doubt, the most important law book that is written by laymen. While it is revised and put forth by a mere handful of men it is in effect the law for all our millions of population. It may safely be said that directly or indirectly it exerts its influence on each and every inhabitant of the United States and its possessions, for they all take medicine. Such a text is to be respected.

The pharmacopoeia lays down standards of purity and of strength for drugs and medicinal chemicals, and by virtue of the Food and Drugs Act these standards become in effect a part of the law. The book tells us what properties characterize preparations for medicinal use, how to make some of the preparations, how to test them, how much of them to take at a dose, etc. No better pharmacopoeia is published and for the greater part of it only praise can be offered. But like everything else artificial in its origin, it has defects, and, as is customary, the virtues will be dismissed with a mere mention, while the defects, or one of them, will be dwelt upon.

I have just said that the pharmacopoeia prescribes for us the quality and strength of our medicines, and how to test them. This statement must be modified. The pharmacopoeia tells us the required strength of practically all the articles within its purview, and tells us how to test *some* of them. The tests given, or, rather, those *not* given at all are the crux of this paper.

Whenever in the text freedom from chlorides, or sulphates, or phosphates, or iron, or most any of the simples is required, the appropriate qualitative test is given. But when it is required to employ a more important test, such as a quantitative assay method, the pharmacopoeia frequently gives no such test at all. Now this really is unfortunate, to put it mildly, for the purity requirements of the book are in the main high, and are all binding on those handling the preparations. If degrees of purity difficult to attain and maintain are required, of course in simple justice methods of ascertaining those degrees of purity should be stated. The selection of methods of analysis at random by different chemists is a poor practice.

The metallic mercury of the U. S. P. is an example of the condition mentioned. Metallic mercury to meet the requirements of purity must contain 99.9 per cent. of mercury. Only one-tenth of 1 per cent. of impurities allowed—and no official assay method given by which to test. This is rather an extreme case, but merely typifies many others. Metallic zinc, practically never taken internally, must contain 99

[1] Read before the Section of Pharmaceutical Chemistry of the American Chemical Society, at Detroit, June 30, 1909.

per cent. of zinc. No method of testing is given; that is, no quantitative method of determining the per cent. of zinc is given. There are many such instances.

We know why the present pharmacopoeia fails in many cases to give these most important methods. At the time the book was published it was not a national legal standard, but became so subsequently, with the passage of the Food and Drugs Act. The need of methods was formerly not so great, and when a relatively simple test such as a volumetric or an easy gravimetric method could not be found, none at all was put into the text. The idea was, also to employ tests requiring the minimum of apparatus and general equipment, on the assumption, it is said, that retail druggists are the principal users of the tests.

So much for the *present* pharmacopoeia—the U. S. P. 8th revision. The book has already been printed and distributed, has been revised and corrected by supplementary circulars, and has nearly served out its time. But what of the next revision, the ninth, the convention for which meets in May next? How shall the question of purity requirements in terms of per cent., and methods of assaying be handled? Are we again to fill the pages with tests for chlorides, etc., and omit the really important and more difficult methods of assay? Are we again to confine ourselves to easy volumetric or gravimetric determinations when there are better and more suitable, though less easy ones, at hand? Are we pharmaceutical chemists willing to be denied the privilege of making use of the latest advances in analytical chemistry? Must we forego the pleasure of using the modern oxidizers such as sodium peroxide and the persulphates? Do we not know the remarkable advances that have been made in electro-analysis? Can we close our eyes for another ten years and bring out a new pharmacopoeia, ignoring all these advantages at our service, and all for the sake of keeping things simple? It does not seem possible to me. In our next pharmacopoeia we need modern methods of analysis. Or at least we should accord ourselves the privilege of using such methods.

To incorporate full quantitative methods of determining gold, mercury, zinc, antimony, and all the others, would enlarge the book very materially, and this is possibly objectionable. For the pharmacopoeia to refer the chemist to some standard *text-book* for methods of analysis would hardly be justifiable or desirable. I suggest therefore that the Committee of Revision of the Pharmacopoeia follow the example of the Department of Agriculture in Washington. As all know this department accepts or adopts the methods of analysis of the Association of Official Agricultural Chemists. Let the Committee of Revision adopt as their methods of analysis the methods of the American Chemical Society. And it will be an excellent beginning for this the new Division of Pharmaceutical Chemistry to investigate, and if possible agree upon some or a few of the methods of analysis now entirely omitted from and so much needed in the United States Pharmacopoeia. Possibly the methods thus worked out and approved by the American Chemical Society could be made sufficiently attractive to tempt the Committee of Revision to use or refer to them.

I therefore offer the suggestion that this Division of Pharmaceutical Chemistry take up the investigation of methods of analysis of pharmacopoeial articles with the idea of selecting what may be termed standard methods of analysis

BOOK REVIEWS AND NOTICES.

Metallography. By Dr. W. Guertler. Volume I. Constitution. Part 1. Berlin: Gebrüder Borntraeger. Price, 4 Mk. 20 Pf.

This is the first part of what promises to be a comprehensive treatise on the subject of metallography. Necessarily future parts must decide as to the merits of the work as a whole, but the first part gives great promise. The chapters are: I, Introduction; II, Constitution in Relation to Temperature; III, Solid Solutions and Compounds; IV, Condition Diagrams; First Group. Paper, typography, illustrations and general appearance are the best.

OFFICIAL REGULATIONS AND RULINGS.

(T. D. 1524.) *Denatured Alcohol.*—Use of specially denatured alcohol prohibited in the manufacture of butyric and formic ether.

Treasury Department,
Office of Commissioner of Internal Revenue,
Washington, D. C., August 5, 1909.

Gentlemen: Your letter of the 31st ultimo, addressed to the chief chemist, and making application for the authorization of formula No. 1 for use in the manufacture of butyric and formic ether, has been received, and the matter given careful consideration by this office.

The fact is recognized that the substances in question fulfil the conditions imposed by the amendatory act in being "definite chemical substances" produced from alcohol by molecular decomposition, and their manufacture from denatured alcohol could lawfully be permitted under Section 40, Part VI of Regulations No. 30.

In view of the fact, however, that these ethers are used mainly as flavoring material in beverages, and the further fact, which is apparent from your communication, that they must necessarily carry a considerable percentage of undecomposed alcohol, I do not consider it to be for the best interests of the Government, or in accord with the spirit and intent of the denatured alcohol law, to permit tax-free alcohol to be used in their manufacture. I must, therefore, deny your application.

Respectfully,
Robt. Williams, Jr.,
Acting Commissioner

Messrs. ————.

Judgment Nos. 92–99, Food and Drugs Acts.

92. Misbranding of canned peaches, plums, pears and apricots (underweight).

93. Misbranding of canned beans (underweight).

94. Misbranding of water (artificially lithiated water labeled as a natural product).

95. Misbranding of canned corn (underweight).

96. Misbranding of a cereal (as to quality and digestive properties).

97. Misbranding of canned tomatoes (underweight).

98. Adulteration and misbranding of syrup (as to presence of maple sugar).

99. Misbranding of syrup (as to place of manufacture and amount of maple sugar present).

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ORIGINAL PAPERS.

ON THE CHEMISTRY OF CERTAIN ALGAE OF THE PACIFIC COAST.

By David M. Balch, S.B. Harv

Received September 13, 1909.

Like most sea-washed regions throughout the world, our Pacific Coast produces many algae peculiar to itself, and some that are more cosmopolitan in character. Some of these are gigantic in size and pelagic as to locality, covering the ocean at about the 10–12 fathom line with dense fields of their floating foliage. Others, of far lesser growth, are littoral, forming in favored localities a dense fringe at about the limit of extreme low tide, and even beneath tidal fluctuations.

It is my purpose in the following pages—after a brief description of some of the most prominent species and varieties, together with their habitat, range, character and general features—to present numerous analyses of the inorganic constituents of each at different stages of their development, and in some instances of different members of each, with remarks on some unexpected results of these researches. Then will follow a dissertation on the economic value of certain of the huge Laminariaceae, and on measures proposed for the exploitation of our marine forests and the utilization of their products for the needs of commerce. The case of kelp *versus* wood as material for distillation will be argued at some length. Also the relative advantages, and disadvantages, that govern the winning of potassium from its ocean sources—unlimited in abundance and ceaselessly renewed—and the exploitation by mining of its terrestrial deposits, which, in certain localities, seem also almost inexhaustible.

A peculiar and most interesting sea-weed, Nereocystis, is found in favorable localities all along the western coast of North America, from warm temperature to subarctic regions. Point Conception, Calif., may be regarded as the boundary roughly separating the southern from the northern species; for, although the species overlap in the Santa Barbara Channel, and the northern species may possibly occur even further south, it does not appear that the southern species has been recognized north of Point Conception.

Whether this plant is an annual or a biennial has been matter for debate, but the question seems merely one of definition; there can be no seasons proper at the bottom of the sea. Commencing life late in the autumn, it perfects itself in the following year, the southern species demanding about 12 months, and the northern about 15 months for its life work. Consequently, it is a plant of very rapid growth, its huge bulk and abundant store of alkaline salts being the product of little more than a single year.

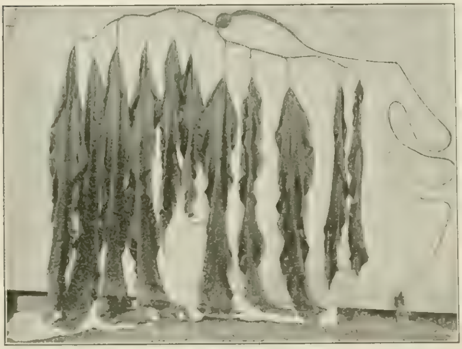
I. Nereocystis gigantea—now better known as Pelagophycus Porra Setchell—is the southern species. Taking San Diego Bay as a center, this plant is fairly abundant for a hundred miles both north and south. Its northern limit has been stated above; its southern is uncertain. It is reported on good authority as growing in company with Macrocystis pyrifera—they usually occur associated—at Mag-

dalena Bay, some 500 miles south of San Diego; it probably grows in localities favoring its increase at many intermediate points.

This plant is popularly known as the "Elk Kelp," from the fact that as it lies stranded on a beach and robbed of its leaves by the action of the surf, the incurved arms garnished with the stout, spiky bases of the petioles, strongly remind one of spreading antlers.

(The accompanying illustration, from a medium-sized specimen in a nearly perfect condition, fairly represents its peculiar form.)

It grows about the 10–12 fathom line from loose rocks, or sunken reefs. When full grown it may consist of a solid cylindrical stem some 60 feet in length by one-half inch in diameter, which, starting from the small, highly-branched holdfast that attaches the plant to its base, abruptly expands near its terminus into a hollow cylindrical slightly



conical tube—named the apophysis—which may exceed 6 feet in length by 3 inches in diameter—separated by a sharp choke, or constriction, from a nearly spherical bladder, which rarely exceeds 8 inches in diameter. No true proportion exists between bladder and apophysis—either may be overdeveloped; they are connected by a short and very narrow internal canal. From a common point at the apex of the bladder issue at nearly right angles two opposite horizontal arms, several feet in length, solid, distinctly flattened, and bearing along their upper edge the petioles of the leaves. The petioles, about six in number for each arm of a mature plant, and separated irregularly by intervals of several inches, are stout at the base but quickly become rounded and very slender; they average 6 or 8 inches in length; each petiole carries a single leaf, but as the petioles are frequently cleft, or divided, near the base, any base may carry two leaves—possibly more. Very rarely specimens have been observed in which the petioles issue alternately from the upper and lower edge of the arm. The leaves differ in shape, size, and texture; these variations may be governed by the progress of their development. The plant as stranded rarely bears even remnants of its immense fronds; or, if the petioles be strong enough to stand the strain, only a few inches of their thick leathery bases—all else has been removed by the surf. The perfect leaves may reach 15 feet or more in length by 20 inches in diameter; they are cuneate at the base, ruffled at the edges, sometimes roughened on the surface by slight spiny projections; often smooth, glossy, and nearly transparent; their color is a rich yellowish brown; the texture sometimes very brittle and flimsy, sometimes comparatively tough. The fluorescence (or sori) occurs in broad dark patches on the leaves.

So much for the mature plant. The infant specimens consist simply of a spherical bladder about 3/4 inch in diameter, crowned by two opposite, short oval leaves, and having a very slender, thread-like stem a few inches in length, terminated by a very small and delicate holdfast; apophysis and arms do not seem to be present even in a rudimentary form. How this fragile little plant can germinate, anchor itself, and grow in the ocean depths, 70 feet beneath the surface, is an interesting matter for consideration. When the bladder has grown to a diameter of about $1^1/_2$ inches the development of its arms is in progress and consists at first of one petiole each with a terminal leaf; their development progresses by fissure of the terminal. The bladder may reach 3 inches in diameter before the apophysis—which is merely a modified form of the bladder, and serves the same purpose, *i. e.*, to keep the plant upright—is much in evidence; then it increases rapidly in size as the needs of the plant demand.

Pelagophycus contains very little cellulose as woody fiber; the bulk of the plant is composed of sound fleshy cellular tissue saturated with saline solutions, and protected by a thin, glossy external bark, or varnish. Approximately some 90 per cent. of its weight is water. When exposed to the sun and wind the plant dries rapidly; the beautiful leaves, after a few hours' exposure, resemble greenish gray tissue paper; stem and arms dry more

slowly but are finally converted into a horny substance, very tough and elastic, and not easily broken across or crushed into pieces. The bladder and apophysis contain no liquid in their cavities; owing to the thickness—from $^1/_2$ to $^3/_4$ of an inch—of their fleshy walls they dry slowly, unless split longitudinally or quartered. When the drying has reached a certain stage these parts become covered with a very heavy saline efflorescence, and to such an extent that when bladders from small plants are dried entire nearly 50 per cent. of the salts they contain are thus exuded. With the stem and arms this efflorescence is much less.

* * * * *

In the following studies of the inorganic constituents of algae, specimens were collected at different stages of growth, and in different seasons of the year. They were dried by exposure to sun and wind until efflorescence commenced, then under glass, and finished at 125° C. A weighed portion was then charred, the char exhausted, and the lixiviate brought to a known bulk in centimeters. From this, measured portions were taken for analysis.

I. Pelagophycus Porra (collected in January, 1905), at a very early stage of growth when the plants lacked apophysis, and in many cases arms.

EXPERIMENT I.

Bladders entire from $1^1/_2$ to $2^1/_2$ inches in diameter were sun-dried under glass; efflorescence was very copious, light and flocculent. They were then broken up, the salts separated by sifting, and drying finished at 125° C. A quantity weighing 1500 grams, was then charred with proper precautions; the char, 939 grams, was packed in a percolator and exhausted with hot water. 2000 cc. extracted 593.5 grams of salts; 1000 cc. additional 114.6 grams; 500 cc. additional 5.7 grams; 250 cc. additional 1.2 grams. The lixiviates, colorless and odorless, were brought to 3750 cc. and were found to contain 715 grams of anhydrous salts. Measured portions were taken for analysis:

		Per cent.
Analysis 1	CO_3 equals	1.01
	SO_4 "	1.33
	Cl "	51.01
	K "	34.91
	Na "	11.74
		100.00

K was det. by platinum—Na by difference.

To the above 1500 grams belong the effloresced salts shaken from it. This was lightly charred to separate a little organic matter, dissolved in water, filtered from a little mechanically mixed sand, and solution brought to 2250 cc. This contained 601 grams of anhydrous salts.

		Per cent.
Analysis 2	CO_3 equals	0.030
	SO_4 "	0.097
	Cl "	47.880

These effloresced salts are nearly C. P. potassium chloride. This most interesting and unexpected result will be considered at length further on.

To determine, then, the constituents of the alkaline salts of the young bladders of the Pelagophycus the above solutions were mixed in proper proportion and 7.92 grams of the resulting salts analyzed as follows:

		Per cent.
Analysis 3	CO_3 equals	0.57
	SO_4 "	0.67
	K "	40.91 (by platinum)

KCl. with a little sulphate. 78 per cent.
NaCl. with a little carbonate 22 per cent.

Consequently, our 2100 grams of dried bladders have given us 1316 grams (62.67 per cent.) of alkaline salts, of which 78 per cent. (1026 grams) is anhydrous potassium chloride. This equals 48.85 per cent. of the raw material. A large trace of iodine—about 0.1 of one per cent.—is also present.

EXPERIMENT II.

The material used for Exp. I, as above stated, came from very young plants. We will now examine the salts yielded by the bladder, 8 inches in diameter, and the apophysis of a large and mature plant, collected Oct. 1, 1907. Cut into slices and dried under glass; efflorescence not flocculent, but crusty—like candied fruit—and somewhat discolored. Salts were removed by light pounding; both salts and residue were dried at 125° C.; they weighed respectively 92 and 315 grams (407 grams of dry material). This was charred and lixiviated as usual and gave 243 grams of anhydrous salts, or 60 per cent. of the material.

The effloresced salts agree closely with Exp. I.

		Per cent.
Analysis 4	CO_3 equals	a trace
	SO_4 "	0.79
	Cl "	47.21
	K "	51 62

KCl. 98.72 per cent. by platinum.

Here again we have nearly pure potassium chloride.

A sample of salts obtained by evaporating the mixed lixiviates gave:

		Per cent.
Analysis 5	CO_3	1.07
	SO_4	1.68
	Cl	47.06

The ratio of KCl to NaCl was found to be as 80 is to 20. Consequently, the 407 grams of material, which gave 243 grams of crude salts, will yield 47.76 per cent. of potassium chloride. Agrees closely with results obtained in Exp. I.

EXPERIMENT III.

Branches.—From a large plant, solid flattened stems having petioles, and small portions of the tough bases of the leaves still attached. Material dried at 125° C. equals 210 grams. Charred and lixiviated as usual gave 104.7 grams salts.

		Per cent.
Analysis 6	CO_3 equals	0.92
	SO_4 "	3.60

As we approach the leaves the percentage of sulphates augments, and we find iodine also increasing. In the salts from bladder and apophysis iodine rarely exceeds 0.1 of one per cent. In the salts from the arms we find 0.328 per cent. Alkaline chlorides are closely as in the preceding analyses. We have then from the arms of the plant 50 per cent. of their weight in crude salts, the value of which is increased by the iodine present.

EXPERIMENT IV.

Leaves.—We now reach the leaves—the laboratory wherein the mysterious, possibly inexplicable, operations of this most interesting plant are carried on, its other members being merely storehouses for their products. Nov. 16, 1906, collected the leaves, nearly intact, from two medium-sized plants, largest 8 feet long, 18 inches wide; a rich golden brown in color, leathery and rather thin; fine print could be read easily through the fresh leaf, which closely resembles corrugated glass. Leaves from one plant darker in color, thicker and apparently more mature. Contained 85 per cent. of water.

617 grams dried at 125° C. gave 174.68 grams of salts (28.31 per cent.) of the following composition:

		Per cent.
Analysis 7	CO_3	0.83
	SO_4	6.77
	Cl	45.72
	K	31.41
	I	0.85

KCl...... 49.24
K_2SO_4.... 12.27 equals 61.51 per cent. potassium salts.

Although the product of crude salts from the leaves is only about one-half that of other members of the plant, their value is much greater on account of their large percentage of iodine.

Thin flimsy leaves, of quite different character, from another plant were then examined with closely approximate results. 115 grams gave 32.65 grams of salts, or 28.40 per cent., composed as follows:

		Per cent.
Analysis 8	CO_3	0.86
	SO_4	7.31
	Cl	44.47
	I	0.875

EXPERIMENT V.

Stem.—All parts of the plant have been examined except the long cylindrical stem, which I have taken up last, because in bulk and weight it is the least important member, and, moreover, can rarely be collected entire. Though apparently solid the stem has a central pith, or core, much softer than the surrounding tissues.

Stems from 10 to 12 feet in length from several young plants were coiled, sun-dried and finished at 125° C. They were then about $^1/_8$ inch in diameter, and very tough and elastic. 90 grams gave 33.76 grams of salts (37.20 per cent.), composed as follows:

		Per cent.
Analysis 9	CO_3	1.81
	SO_4	7.66
	Cl	42.71
	I	0.55

To the above observations on Pelagophycus porra will be appended some remarks on the distribution of iodine; and also on the inorganic constituents insoluble in water—the true ash. We now pass to the northern representative of these giant Laminariaceae.

II. Nereocystis Leutkeana.—Commencing a little south of Point Conception, California, and extending into the Arctic and even to the shores of Kamtschatka, we have in this plant one of the most common and interesting algae of our north Pacific coasts. It is present everywhere, whether obstructing with its growth bays and island passes, or torn loose and wave-tossed, or stranded on their shores. Firmly anchored at a depth of from 8 to 10 fathoms by its branching holdfasts to submerged reefs, or scattered rocks, it covers with its streaming strap-like fronds patches acres in extent so densely as to impede navigation. That this plant differs greatly in form from the southern species is evident from the illustration.

(Photograph of specimen from San Juan Island, Puget Sound, opposite page.)

Its slender whip-like stem, the upper one-third of which becomes hollow and gradually expands in diameter from less than $^1/_2$ to 3 or 4 inches, terminates in a small oval bladder separated from the stem by a slight constriction. In an average plant the solid portion of the stem may be 40 feet, the hollow part—the apophysis—about 20 feet in length, the bladder 4 or 5 inches long and about 3 inches in diameter. The huge branching arms, that

carry leaf petioles, so conspicuous in Pelagophycus, are entirely lacking. Its small oval bladder is crowned by a dense mass of narrow fronds which vary in length from 10 to 30 feet. It forms asexual spores in great numbers on the surface of its fronds from August to December in localties about Puget Sound. Its period of growth comprises about 15 months; germinating in the autumn, it perfects itself about the close of the following year.

EXPERIMENT I.

Effloresced salts, from specimens collected at San Juan Island, Puget Sound, about June 1, 1907, were first examined. These had fallen from air-dried material and were mixed with a little organic matter; they were lightly charred, dissolved in water, the solution filtered, and evaporated to dryness. The specimen thus obtained was purely white, weighed 197.8 grams, and had the following composition:

		Per cent.
Analysis 10	CO_3	0 082
	SO_4	0 090
	Cl	47.740

Consequently, we have here potassium chloride—a crude and unpurified product—that very nearly reaches the requirements of a C. P. article. Not a trace of iodine was present, but sodium and magnesium could be recognized.

EXPERIMENT II.

Bladder and Apophysis.—The specimen examined was collected about October 1, 1906, and sent me, undried, from Seattle, Washington, by express. It was evidently stranded, for the leaves were fragmentary and much decayed; the hollow portion of the stem—which carried a very small oval bladder—measured 15 feet in length; the solid part 25 feet.

The hollow portion effloresced very strongly during the drying, and when finished at 125° C. weighed 262 grams, which yielded 153 grams of salts, or 58.51 per cent. of its weight. Composition as follows:

		Per cent.
Analysis 11	CO_3	0.026
	SO_4	1.180
	Cl	48.580
K plus Na		50.220

The ratio of K to Na was found to be nearly as 80 is to 20. Iodine was present slightly exceeding 0.1 of one per cent.

EXPERIMENT III.

Stem.—The solid portion, 25 feet in length, of the stem of the above plant furnished 171 grams of dried material, from which 57.3 grams (33.51 per cent.) of salts were extracted.

		Per cent.
Analysis 12	CO_3	4.41
	SO_4	3.92
	Cl	42.15

Iodine, two determinations, 0.39–0.41 per cent.

In the condensation of iodine in the solid portion of its stem, this plant agrees with its congener, Pelagophycus, and, as will be shown further on, this feature is common to most of the hard-stemmed algae.

EXPERIMENT IV.

Leaves.—The leaves from Experiments 2 and 3 being badly decayed and not fit for use, others (fragmentary) collected from young plants about June 1, 1907, at San Juan Island, were utilized. Dried at 125° C., they weighed 607 grams. Charred and lixiviated, they gave 270.3 grams of salts, or 44.53 per cent. composition, as follows:

		Per cent.	
Analysis 13	CO_3	0.52	
	SO_4	5.26	
	Cl	46.52	
	I	0.117	
	K	36.55	det. by platinum

Total potassium salts equal 71 per cent.

On comparison with Analysis 7, it will be seen that the amount of crude salts from leaves of N.

Leut. is more than 50 per cent. higher than from those of Pelagophycus, or as 44.53 is to 28.31. Also that their percentage of potassium is higher as 71 is to 61.5, while iodine is present only as 0.117 is to 0.85. But the leaves of Pelagophycus came from a fine mature specimen collected in November, while those from N. Leut. were from young undeveloped plants collected late in May. Consequently, comparison is faulty, and this matter will be settled by further investigation as soon as mature leaves can be obtained. The increase in sulphates and the storing of iodine in the solid stem both warrant the expectation of a higher percentage in mature leaves.

III. Macrocystis pyrifera.—Unlike the preceding, this huge and vigorous plant enjoys a very wide range, and seems indifferent as to temperature. Along our coast it extends from Magdalena Bay, Mexico, to Sitka, Alaska; on the South American coast it abounds throughout Fuegia and around Cape Horn and extends north well up toward the equator. It is abundant on the coasts of New Zealand, the southern coasts of Australia, and of scattered islands throughout the Antarctic Ocean. Different species may be noted, but as yet the northern and southern species are considered to be identical.

This plant differs greatly, both in habit and appearance, from the Nereocystes. In localities favoring its growth it forms a dense belt, or grove, covering the surface of the ocean about the ten-fathom line with broad meadows of its graceful foliage. Anchored by its immense holdfast, which may exceed 3 feet in diameter, it quickly branches into a large number of round solid stems, usually less than one-half inch in diameter, and often far exceeding 50 feet in length. From these stems alternately, and at distances usually approximating six inches, grow pear-shaped bladders measuring—according to the development of the plant—from $^1/_2$ to 1 inch in diameter, and from 2 to 4 inches in length; the upper, or bulbous, part of the bladder is crowned with a single lanceolate leaf, from 1 to 2 feet in length, beautifully proportioned, and of a rich yellowish brown. According to general statement, the spores—sori—occur on submerged, bladderless leaves near the holdfast.

This plant is doubtless perennial, though its life may not extend over many years. It attains great bulk and weight. Detached leaves and branches are constantly brought to shore by the surf; during rough weather it is often stranded in vast quantities, and entire plants many hundred pounds in weight strew the beaches; these usually include plants of Pelagophycus in their tangled masses, but they are never entire. Its texture throughout is much tougher than in the Nereocystes, and there is a lower percentage of water in its tissues. Its leaves develop in drying an odor as peculiar, and almost as agreeable, as that of new-mown hay—a characteristic odor that is permanent.

Macrocystes, then, consists of three principal parts—the stem, the bladder and the leaf. These were taken from a large, mature, plant—collected October, 1907—dried as usual and examined separately. From the material, about 1600 grams in all, a small deposit of effloresced salts fell during the drying.

EXPERIMENT I.

Effloresced salts, charred, dissolved, filtered and evaporated; weighed 43.25 grams; analysis as follows:

		Per cent.
Analysis 14	CO_3	0.087
	SO_4	0.590
	Cl	47.710

No iodine: faint trace of Mg.

Here again we have nearly pure potassium chloride.

EXPERIMENT II.

Leaves.—These were fragmentary, and mostly from the basal portion of the leaf next the bladder. 297 grams, treated as usual, gave 64.7 grams of anhydrous salts, equal 21.80 per cent.

		Per cent.
Analysis 15	CO_3	1.80
	SO_4	11.20
	Cl	40.44
	I	0.70

EXPERIMENT III.

Bladders.—These varied in length from 3 to 4 inches, and were nearly 1 inch in diameter. 565 grams gave 232.5 grams salts, or about 41.15 per cent.

		Per cent.
Analysis 16	CO_3	1.08
	SO_4	3.15
	I	46.96
	C	0.54

EXPERIMENT IV.

Stems.—About $^1/_2$ inch in diameter. 688 grams, treated as usual, gave 201.75 grams salts, or 29.32 per cent.

		Per cent.
Analysis 17	CO_3	3.96
	SO_4	5.08
	Cl	42.12
	I	0.64

Iodine is very evenly distributed throughout the tissues of this plant.

The solutions were mixed in proper proportions and analyzed:

	Per cent.
CO_3	2.38
SO_4	4.91

Carbonate and sulphate were then changed to chloride and potassium determined by platinum:

		Per cent.
Analysis 18	Cl	50.81
	K	39.41

The potassium salts present in the crude salt from Macrocystis are as follows:

	Per cent
KSO_4	8.79
KCl	67.76
	76 55

The leaves were fragmentary; had they been intact the amount of sulphate would have been somewhat larger and the chloride less.

The following analysis is from perfect leaves of a smaller and less mature plant:

		Per cent.
Analysis 19	CO_3	3 43
	SO_4	12.50
	Cl	38.05
	I	0 507

Three branches with perfect leaves from a young plant were dried. Stems and bladders equaled 730 grams; leaves 2100 grams. The proportion varies, but the leaves may be regarded as forming from two-thirds to three-fourths of the entire weight of the plant.

A careful study of the results of the foregoing analyses leaves us face to face with certain problems of much interest to science, but not easy of comprehension and difficult to explain. It will be noted that these algae, particularly Pelagophycus and Nereocystis, are very rich in potassium chloride—their tissues are gorged with this salt; and this is true not only of the mature plant—when it has attained great bulk and weight, produced its spores, and accomplished its life work—but of the infant plant, just entering life, consisting of little more than two small leaves and a bladder weighing a few grams, which is even richer in potassium.

The comprehensive analysis of sea-water by Dittmar, from specimens collected by the Challenger expedition, assigns to it the following composition. Sp. Gr. 1.026. In 100 parts of water 3.5 parts of salts, as follows:

NaCl	77.758	Also traces of Br, I, Fl, P, Si, Au, Ag, Pb, Cu, Zn, Co, Ni, Fe, Mn, Al, Ba, Sr, Li, and other elements.
MgCl	10.878	
$MgSO_4$	4.737	
$CaSO_4$	3.600	
K_2SO_4	2.465	
MgBr	0.217	
$CaCO_3$	0.345	
	100.000	

It will be observed that potassium sulphate is present in sea-water in the proportion of about 2.5 per cent. of 3.5 per cent., or 0.087 per cent., which very nearly equals 0.04 or $^1/_{25}$ of one per cent. of potassium.

Although growing in a medium in which sodium abounds, the algae assimilate the far less abundant potassium, preferably as chloride; and, as seems probable without modification, for the organic acids of the plant are chiefly contained with Ca and Mg.

A phenomenon of much interest is the extrusion of potassium chloride, in a state of almost chemical purity, through the skin, or outer tissue, of the drying plant. The salt does not appear until drying is far advanced and the skin of the bladder has become soft and pliable, when it passes rapidly as a light, flaky efflorescence; which, if the material is protected under glass, may reach half an inch in thickness. The composition of the effloresced salts is given in Analyses 2 and 4, and of the crude salts from which they come in Analyses 3 and 5. But Analyses 3 and 5 do not give correctly the composition of the saline solution from which the salts effloresced; they give its composition after carbonization and lixiviation of the charred tissues that contained it. Before these processes its composition was far more complex, inasmuch as organic compounds of calcium, magnesium, sodium, phosphates, and other matters were present.

In the case of Nereocystis, the stems from several large plants, not sufficiently dry to have become brittle, were headed up in a barrel where they remained for nearly two years. On removing the material a few pounds of effloresced salts remained, shaken off during the operation. Their composition is given in Analysis 10, the composition, after carbonization, of the crude salts whence they came in Analyses 11 and 12.

And, again, from Macrocystis. The extruded salts come from the bladders and stems, the leaves do not effloresce; their composition is shown in Analysis 14; that of the saline mixture, after carbonization, from which they come in Analyses 16 and 17. It will be noticed that these show a far larger proportion of alkaline carbonate and sulphate than the preceding, nevertheless their effloresced salts are equally pure.

These natural processes, and their results, are not easy to comprehend or explain. They remind one of the operations of osmosis or dialysis, but results thus obtained by no means correspond as is shown by the following experiment:

A quantity of dried material was ground to a coarse powder, mixed to a thin paste with water, and dialyzed through parchment paper. The

liquor from the outer vessel, evaporated to dryness, yielded a yellowish granular salt; 9.56 grams were taken for analysis. Heated to incipient redness, they blackened and considerable organic matter burned off; they were then dissolved in water and solutions and washings brought to 250 cc. Carbonaceous residue on filter was incinerated and gave 0.092 g. of gray ash consisting chiefly of phosphate of lime and magnesia. The solution had the following composition:

		Per cent.
Analysis 20	CO_3	0.13
	SO_4	0.35
	Cl	50.51

The organic matter burned off weighed 0.83 gram. The proportion of chlorine denotes the presence of about 25 per cent. of sodium chloride. On the whole, salts obtained by dialysis differ essentially from those extruded by the drying plant.

The percentage of sulphuric acid has a wider range than any other constituent of the soluble salts of the algae; less than one per cent. is often present, but I have recognized as high as 47.50 per cent. in the crude salts of a certain rockweed. Its proportion varies greatly in different members of the same plant, a fact everywhere apparent in the preceding analyses. It usually predominates in the leaves. Many algae rich in sulphates are correspondingly rich in iodine, but there are many exceptions.

I have given in the foregoing pages a concise description of the range, relative abundance, life habits, and chemical composition of our three most prominent giant kelps. It now remains to consider their economic value, and the most practical methods for the utilization of their products. It will have been noted that they all abound in potassium salts; that their brief life seems devoted to the task of extracting these salts from the medium in which they grow and storing them in their tissues; that they provide potassium compounds in a state of purity directly suited to our needs.

If we trace potassium to its source we shall find it in the feldspars present in all primitive, or igneous, rocks. Common granite contains about 40 per cent. of feldspar—about 7.5 per cent. of alkalies: gneiss, mica, slate, syenite, etc., are analogous in their composition. Potassium, in addition to its many uses in the arts, is indispensable as a food producer; any source from whence it can be easily and abundantly obtained is of vast importance to humanity. Its natural sources are obvious—feldspathic rocks, deposits of mineral salts, growing plants. Since feldspar is everywhere, and contains some 15 per cent. of potassa, why not seek it directly at its source? Because the extraction of potassium from orthoclase, common feldspar, is too difficult and expensive to be practicable. The second source is deposits, beds of natural salts in some localities of vast extent. Our third source is growing plants; and as, obviously, for many reasons land plants are not available as material, we turn to the ocean forests, to marine plants, for our supply. The ocean is a vast reservoir for potassium salts dissolved by the action of the elements from the rocks and carried by the rivers to the sea. They have accumulated there for ages; and, although potassium oxide constitutes but one-twenty-fifth of one per cent. of the weight of sea water—about eleven ounces in a cubic yard—if we take the trouble to calculate the number of cubic yards in a single cubic mile of ocean water, we regard with amazement the mass of potassium oxide contained therein; it is as limitless and inexhaustible as the nitrogen of the atmosphere. If by any means at our command we attempt to extract the dozen ounces of potassium contained in each ton of sea water, we shall find ourselves engaged in a difficult and unremunerative endeavor which we cannot successfully accomplish.

But our marine forests are quietly and ceaselessly accomplishing this task for our advantage. Each plant of the giant kelps stores up yearly, in addition to other valuable products, potassium chloride most liberal in quantity, and of remarkable purity, as the result of a natural process. We have but to gather the plant and utilize its products. If we are not wise enough to do so, the plant having reached maturity decays, its products return to the ocean, are taken up by its successors in the ensuing year, and the opportunity is ours once again.

In the matter of the utilization of the kelps on a large scale for the demands of commerce, two subjects for discussion come next in order:

I. How the raw material can be gathered and handled most conveniently. II. How its several products can be most advantageously extracted. The first is the more important, for on it largely depends the financial success of the enterprise.

I. Gathering the Kelp.—Certain seaweeds—notably Laminaria saccharina—have for ages found their uses whether as applied directly to the soil for fertilizing material, or in supplying crude raw material on a small scale for certain branches of

manufacture. This industry was confined to countries where labor was cheap, and to seasons of the year when there was little else to do. The plant was cut by hand from outlying reefs and brought to land by boats, or collected where it lay stranded in masses after heavy gales. In either case the material was spread in a convenient place, dried as thoroughly as the weather permitted, drawn into heaps, and burned, the very impure ash resulting was used as a basis for manufacture. The whole process was unscientific, crude, wasteful, and costly in the highest degree; and nothing but the high prices obtained for the several products could have justified such methods. At the present day steam power must be substituted for hand labor, and the sources of waste closed.

A steam scow, or launch, properly fitted with labor-saving appliances, would seem to be the best vehicle for gathering and transporting kelp. It could move quickly from place to place, select the best fields for its operations, cut the plant, draw it on board, carry to shore and unload its cargo—all by steam power and at minimum cost—for, inasmuch as a dredge can raise a cubic yard of silt or sand from a considerable depth and transport it where needed at very moderate cost, there is no reason why a properly equipped craft cannot handle a ton of seaweed to equal advantage.

Handling the Material.—Let us suppose that a cargo of kelp has been landed at the wharf of a drying shed; the next step is to get it into condition for transportation. Freshly lifted from the sea the plant contains from 85 to 90 per cent. of water, is heavy, bulky, and unmanageable, and must first of all be deprived of its superfluous moisture. Though drying progresses very rapidly under the influence of sunshine and wind, in many points this method is objectionable. Drying by artificial heat is to be preferred, and there are methods in common use, perfectly applicable to seaweed, by which large masses of coarse material are easily and cheaply desiccated. If the material is to be transported—for instance, from several drying sheds at long intervals to a central manufacturing plant—drying should not be pushed too far, but stopped when an efflorescence of salts begins to appear the material is then soft and pliable, and can be pressed, like hay or cotton, into small space; a ton of wet kelp can thus be reduced to a small bale weighing not more than 250 pounds, in which form it is easily transportable and its contents will keep indefinitely, unchanged and without loss. If drying be carried too far, efflorescence is profuse, the material becomes too tough and elastic to be easily managed, and there is considerable loss in the handling.

II. Treatment of the Dried Material for the Extraction of the Several Products.—Kelp, dried and handled as mentioned above, still contains some 15 per cent. of water. The alkaline salts—chlorides, sulphates, iodides—which constitute from 40 to 50 per cent. of its weight are contained in much vegetable tissue. When inorganic matters unaffected by moderate heat are to be separated from organic, our most obvious course of procedure is to decompose the latter by burning. This process is best carried on by dry distillation, for in this way we can collect, or utilize, products of value both condensable and non-condensable arising from the decomposition of the organic matter.

The distillation of wood—as now largely practised in many countries—may be cited as an example of the progress and results of this operation. Well seasoned, air-dried wood, of any hard variety, is heated in suitable containers; decomposition begins at about 150° C. and is practically complete at 430° C. The chief products are formed continuously throughout the entire process, which proceeds in three characteristic periods: from 150° to 280° acetic acid, methyl alcohol, and wood creosote are the chief products; from 280° to 350° large volumes of gases are given off; from 350° to 430° solid hydrocarbons are distilled. Additional volatilization can be obtained by increased and protracted heating, but only to the extent of about 1.5 per cent. It will be noted that a very moderate heat—not much above the melting point of lead, 325° C.—is sufficient for the greater part of this operation.

The behavior of kelp under similar treatment is analogous but by no means parallel, nor are its products the same. In the distillation of wood the main products are the condensable volatile substances; the charcoal is of little consequence. With kelp it is just the opposite; the char saturated with mineral salts is by far the most important product of the operation. From wood, the watery parts of the distillate are acid; from kelp they are neutral, or slightly alkaline, proving the presence of ammoniacal compounds. In other respects the condensed products are approximately the same.

In the case of wood, complete volatilization is of little consequence; charring need not be perfect; with kelp it must be absolutely so, for, if the

char holds unexpelled any portion of the organic products of decomposition, the lixiviates from such char will not be odorless or colorless, and consequently of little use for the production of pure salts. Fortunately, this perfection of the char can be ensured by certain modifications of the process; lixiviates from such a char will yield colorless salts of any degree of purity desired. All iodine present can be easily recovered from the waste liquors of the several operations.

Kelp versus Wood.—Let us now consider the case from the practical and commercial point of view, and compare the results to be expected from the similar handling of a weighed quantity of each of the above natural products.

Hardwood—preferably beech—selected where it most abounds, is cut, split, stacked—all by manual labor—seasoned for at least a year, and then transported to the plant for distillation. Kelp is cut, loaded, landed, dried and baled—all by the best mechanical labor-saving appliances; and then in a compact and easily handled form transported to the plant for distillation. Both, save for a necessary, but inexpensive, modification in the case of kelp, are treated alike and at the same cost of manufacture.

One ton of thoroughly dried beechwood gives an average yield of 120 pounds of dry calcium acetate, 8 gallons of tar, 6 gallons of alcohol and acetone.

These, which may have a commercial value of some six dollars, represent all the products usually marketed from a ton of dry wood; the charcoal—some 30 bushels—and gases resulting from the operation are utilized as fuel in the establishment.

The condensed products from the distillation of kelp are analogous to those from wood, and may be regarded as approximating them in value. But here all comparison ceases; the non-volatile portion, the charcoal saturated with alkaline salts, is by far the most important product of the process.

One ton of thoroughly air-dried kelp, in addition to valuable by-products volatile and non-volatile, may be depended on for a minimum yield of 500 pounds of pure potassium salts, 3 pounds of iodine.

These are worth above twenty dollars in the markets, and the presumptive value of the several by-products should warrant the statement that the average yield of a ton of air-dried kelp may be stated at twenty-five dollars ($25.00)—an average which is far more likely to be exceeded, especially as regards iodine, than reduced in quantity or value.

How much more promising then in its returns is the distillation of kelp than that of wood. Nevertheless, wood is largely and profitably distilled for its volatile products alone.

One other source of potassium remains to be considered. There exist in certain localities vast beds, or deposits, of mineral salts that carry a large percentage of potassium. These mines are at the present time actively operated and yield a large proportion of the potassium compounds in commerce; their output of low-grade manurial salts for agricultural purposes is immense, and, both as regards quantity and cheapness, beyond competition. But with the purer salts which the numberless claims of manufacture and the arts demand, this is by no means the case. The preparation from their ores of a pure potassium chloride or sulphate is a laborious and expensive operation, and there are no by-products of consequence to reduce the cost of manufacture. But their preparation from kelp presents no difficulties; it yields no rough, complex material so difficult of refinement, for its crudest salts are well on the way toward purity, and can furnish abundantly and cheaply any perfected product that commerce may demand. And again, the by-products from kelp are of prime importance both as regards quantity and value; there is little doubt that they can be made to pay the entire expense involved from the gathering of the raw material to the marketing of its products. Consequently, potassium salts manufactured from kelp should be able to compete in price with any similar products wherever or however produced.

Another most important product of the algae is iodine. This element, of wide use in therapeutics and the arts, was formerly extracted from marine plants; since its discovery in the mother liquors of the purification of Chili-nitre commerce has been supplied chiefly from that source. But the vast deposits of Chili are being rapidly exhausted; their complete extinction is plainly in sight; a few years hence we must look again to the ocean for the world's supply of iodine.

This element, like gold, is present in sea water in infinitesimal proportion. Certain marine plants extract it eagerly, no one can explain how nor why. Two plants are growing side by side on the same stone; in habit, growth and external appearance they are very much the same, but in one of them we find iodine astonishingly abundant, while the

other contains not a trace. The ocean is an inexhaustible treasury of varied wealth, but its riches are stored in so attenuated a form that we are powerless to gather them without the aid of natural processes that go on continually. Marine plants include annually certain portions of this wealth, and offer it for our acceptance like dividends due; should we refuse, it is returned to the treasury, and as time advances offered us again and again.

Nevertheless, the old proverb "vilior alga" still holds good; our marine crop is despised and rarely harvested; in speaking of the vegetable growths of the sea the term "weed" is universal. A weed, according to the best definition ever given, is a plant whose virtues yet remain undiscovered. It is fitting, then, that the more prominent members of the numerous genera and species of these plants be studied, and their hidden virtues brought to light.

Assuming it to be not impossible—though by no means probable—that a marine plant may be found sufficiently complacent to have included and stored up gold in its tissues; that such a plant would be widely sought and cultivated there is little doubt. But products of more substantial value to us than gold, by processes that we cannot imitate, are being prepared and stored for us yearly by plants that we at present despise. They draw these products from a source unquestionably inexhaustible. This term is often loosely applied to sources that by no means deserve it; we observe the vast gold reefs of the Rand, and say here is an inexhaustible field for exploitation; we consider the extensive saline deposits of Germany, and repeat the remark; a generation ago we were saying the same of the nitre beds of Chile; that no terrestrial deposit of value can escape depletion the fate of the latter proves.

But with the saline contents of the ocean it is different. They are not only as now existent inexhaustible, but are being constantly augmented, for as long as rain falls on disintegrated rock and its surplus flows into the sea the mineral contents of the ocean will increase.

Every economist views with disfavor the extravagant—in fact criminal—wastefulness of cities great and small, through whose sewers the fertility of a million acres is poured yearly into the sea. The phosphoric and nitrogenous constituents of this waste seem hopelessly lost; but potassium, one of the most important, we can easily recover, for along our coasts are growing with the rapidity and vigor of the bamboo countless millions of marine plants, each one of which may store up during its short life from one to two pounds of chloride and sulphate of potassium.

We are dependent for our food supply on the fertility of our soils; in order that they may remain productive the constituents that make them so—removed with each annual crop to distant localities—must be supplied from other sources. The chief of these are phosphates, combined nitrogen, and potassa. The first is supplied by animal waste, and by mineral deposits fairly abundant; the atmosphere is a vast reservoir of nitrogen and oxygen uncombined, which we are rapidly learning how to economically combine to produce the products we need; that we can economically win from a similarly inexhaustible source the third element we require, I have endeavored to make plain in the preceding pages.

This paper will be followed by a second on the chemistry of the more important littoral algae, many of which are of interest, and on some other results of the study of marine growths.

I take this opportunity to express my obligation to the courtesy of Prof. Setchell, of the University of California, and to Prof. Frye, of Washington, for valuable information on the nomenclature and habits of these plants.

CORONADO BEACH, CALIF

NITRATES IN BOILER-WATERS.

BY GEORGE S. JAMIESON.

Received October 28, 1909.

The determination of nitrates in the analysis of waters to be used for boiler purposes does not appear to be customary, and, indeed, such determinations may be considered unnecessary in cases where potable waters containing only traces of nitrates are under consideration. However, it sometimes happens that manufacturers, in order to save the cost of city water, employ for this purpose ground waters from densely inhabited districts, and in such cases, where nitrates may be comparatively abundant, their determination is believed to be important.

For the last five years the writer has made it a practice to determine nitrates in boiler waters by means of the well-known colorimetric method used in sanitary examinations. Several ground waters have been analyzed which caused severe corrosion as well as a heavy scale in the boilers, and the conclusion was reached that the nitrates were largely

responsible for the corrosion, on account of their oxidizing action at the high temperature reached by the metal in the presence of heavy scale.

A particular instance of a water from a driven well in the city of New Haven may be mentioned. After this water had been used for a short time the boiler tubes were filled with small holes, and were coated with a very thick and hard irregular scale. The water gave the following analysis:

	Parts per million.
Sodium chloride	85.7
Sodium nitrate	26.8
Potassium nitrate	28.1
Magnesium nitrate	99.6
Calcium nitrate	83.0
Calcium sulphate	117.0
Calcium carbonate	25.0
Iron carbonate	9.5
Silica	20.0

The quantity of nitrates (182.9 parts per million of NO_3) in this water is very great and although nitrates are very soluble in water, they would not fail to be deposited in the hot scale wherever the water penetrated into it. In fact, small quantities of nitrates were found in the scale itself of this boiler, although they must have been destroyed by heat in the parts of the scale next to the metal.

Another well water from a different locality in New Haven was found to contain 39.85 parts per million of NO_3, besides large amounts of carbonates and sulphates. This was not recommended for boiler purposes. Both of these well waters were characterized by being very free from organic matter and were neutral in reaction after the carbon dioxide had been boiled off.

	Parts per million.		
No.	Total solids.	Chlorine.	Nitrate NO_3.
1	331.00	25.00	55.35
2	346.00	22.00	44.30
3	85.00	9.00	20.68
4	266.00	23.00	54.47
5	185.00	9.00	20.37
6	243.00	26.00	31.62
7	301.00	23.50	68.20
8	434.00	58.00	59.78
9	106.00	11.00	8.85
10	345.00	25.20	56.07
11	172.00	7.25	39.85
12	261.00	22.00	44.30
13	81.00	9.00	17.71
14	119.00	12.75	17.71
15	220.00	20.00	66.44
16	95.00	6.00	15.58
17	257.00	12.00	17.71
18	164.00	14.00	44.30
19	170.00	11.00	22.14
20	275.69	11.42	13.00

Further investigations are needed to reach a decision in regard to the amount of nitrates that may be permissible in a boiler water, and also in respect to the protective effect of other constituents.

The table of analyses given above comprises twenty waters from Connecticut, and serves to show the abundance of nitrates in them.

As a comparison with the large quantities of nitrates shown in this table, it may be observed that the average amount of NO_3 in the water supplies of Connecticut cities is only about 1 to 3 parts of NO_3 per million.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.

CRUDE PETROLEUM AS A REDUCING AGENT FOR ZINC ORES.

By HARRY H. HUGHES AND HARRISON HALE.

Received September 17, 1909.

The process generally in use for zinc reduction is exceedingly cumbersome, slow and far from satisfactory. Comparatively small quantities of the roasted ore are mixed with coke and coal and heated in clay retorts which must necessarily be of considerable thickness, the zinc distilling over. The time required is about twenty hours and the expense for heat large. In the best of coals there is quite an amount of matter which does not act as a reducing agent. Some of this is not only not helpful to the process but really injurious, as oxygen is furnished which hinders the reduction. These impurities also occupy space in the retort and consume heat the same as ore.

The high percentage of carbon and of hydrogen in crude oil and its resulting reducing power suggest it as a possible reducing agent. Its extreme cheapness makes it all the more desirable. An objection to its use arises at once in the fact that a temperature of at least 1200° C. is required to practically reduce zinc oxide to metallic zinc and before such a temperature could be reached in the usual furnace all the oil would be volatilized, leaving an insufficient amount of carbon to carry on the reduction. Evidently, then, if crude oil can be used economically for zinc ore reduction it must be in a continuous process by which the furnace can be heated to a sufficiently high temperature and the mixture of oxide and oil fed into it. It would seem that under such conditions reduction should take place before any quantity of the oil can escape. To test this assumption a series of experiments was carried out in this laboratory.

An ordinary gas pipe, 3/4 inch in diameter, was connected at right angles with a cup from which

the mixture of ore and oil could be fed by means of a cock. At first this pipe was placed in a Bunsen combustion furnace but no reduction occurred as the necessary temperature could not be reached. It was then passed through a Brown assay furnace, entering through a hole cut in the back and passing out the door with the end nearer the cup being slightly elevated. The coke fire around this gave ample heat without the use of a blast. The pipe extended some inches from the furnace acting as a condenser.

Fifty grams of zinc oxide mixed with enough oil to make it pass through the cock was the usual charge. The oil required for this was in considerable excess of the amount needed for reduction. So-called "black oil," the crude with kerosene and the lighter oils removed, was used at first and later the regular crude; either will answer.

After the furnace was heated the charge was run in. An effort was made to pass it in slowly, but with this rough apparatus usually without success as almost the entire charge passed in at once. An evolution of gas from the oil on the heated surface followed. The charge remained in the heated pipe for twenty to thirty minutes when the pipe was removed and cooled and the contents examined. Beautiful specimens of zinc were found in the condensing portion of the pipe and there was an almost complete absence of "blue powder."

Some of the zinc was feathery as if both the oxide and the oil were in a volatile state when reduction occurred. This reduction in a gaseous condition greatly shortens the time required as the reducing gas is in immediate contact with the oxide to be reduced.

The gas generated by the excess of oil together with the carbon monoxide formed in the reduction was frequently lighted as it passed out of a burner connected with the end of the pipe. It should be possible to use the gases to heat the pipe or other retort containing the charge, largely reducing the fuel expense.

A number of trials were made with uniformly good results. From our experiments we conclude:

First, that zinc ores can be successfully treated, after roasting, by using crude petroleum as a reducing agent.

Second, that the theoretical advantages from the high reducing power of the oil and from the gaseous state of oxide and reducing agent, hold in a practical test.

We believe further that a continuous process based on these principles would be much cheaper, more rapid and more easily controlled than any process now in use. Arrangements have already been made for trying out the process on a large scale using the continuous process furnace devised by one of us.[1]

WHITCOMB CHEMICAL LABORATORY,
DRURY COLLEGE
SPRINGFIELD, MISSOURI.

TINCTURE OF IODINE.

BY AZOR THURSTON.

Received July 31, 1909.

Prior to the last edition of the *United States Pharmacopoeia*, tincture of iodine consisted simply of iodine dissolved in alcohol. Owing to the rapid loss of free iodine by the formation of either ethyl or hydrogen iodide the pharmacopoeial standard has been changed, by the addition of potassium iodide, to prevent the conversion of the free iodine into iodides.

In the assay of the tincture determinations should be made for iodine, potassium iodide, ethyl and hydrogen iodides, and alcohol.

Iodine is determined by the well-known U. S. P. method by titrating five cubic centimeters with decinormal thiosulphate solution, whereby sodium iodide and sodium tetrathionate are formed: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. The number of cubic centimeters decinormal sodium thiosulphate used multiplied by 0.01259 will give the amount in grams of free iodine in 5 cc. of the tincture, and by multiplying the product by 20 gives the number of grams of iodine per 100 cc.

Potassium iodide is estimated according to La-Wall[2] by evaporating the tincture on a water bath, adding several small successive portions of water, drop by drop, to aid in volatilizing the last portions of the iodine, and weighing the white crystalline residue in a tared watch-glass, which should be used for the experiment.

The writer prefers to determine the potassium iodide as follows: Place 5 cc. of the tincture in a platinum crucible and add 2 cc. dilute sulphuric acid; evaporate on a water bath until the alcohol and most of the free iodine are volatilized, then heat to dryness over direct flame, ignite to whiteness, cool and weigh. The residue will consist of potassium sulphate, and the weight obtained multiplied by 1.9 will equal the amount of potassium iodide

[1] Hughes, *Mining World*, July 10, 1909.

[2] *Proc. A. P. A.*, **1907**, 159.

present in 5 cc. of the tincture; this product multiplied by 20 will give the quantity in grams per 100 cc.

Ethyl and Hydrogen Iodides.—A number of methods have been suggested to determine iodine in mixtures containing free iodine, iodides, bromides and chlorides. In nearly every case some manner of liberating the total amount of combined iodine, existing as iodides, and finally estimating the free iodine with sodium thiosulphate, has been recommended. The free iodine, having been determined in a separate portion, is deducted from the total amount of iodine, the difference being the amount of iodides present.

The majority of the methods are applicable in the assay of tincture of iodine, by first determining the free iodine and potassium iodide, as has been outlined, and then estimating the amount of total, combined and free, iodine in the tincture by one of the methods to follow; the iodine in the free state and that existing as potassium iodide is deducted from the total iodine found, and the difference is the amount existing as either ethyl or hydrogen iodide.

Richard[1] determines the amount of free iodine in 10 cc. of the tincture with sodium thiosulphate in the usual manner and then adds a two per cent. solution of potassium iodate; the coloration produced is decolorized with sodium thiosulphate solution. The difference between the thiosulphate solution necessary to decolorize the original tincture and that required to decolorize it after the addition of potassium iodate indicates the amount of hydrogen iodide present.

Cook[2] proposes the addition of hydrogen peroxide to a solution of iodides acidified with acetic acid. Thus the iodine is liberated; the iodine extracted with chloroform and titrated in the usual manner.

Villiers and Fayolle[3] proposed to liberate the iodine from iodide with a solution of ferric chloride, extracting the free iodine with carbon bisulphide, and treating with sodium thiosulphate.

Barrie[4] liberates the iodine with a 5 per cent. solution of potassium bichromate and a 10 per cent. solution of sulphuric acid, extracts the free iodine with toluene and titrates as usual with sodium thiosulphate.

[1] *Proc. A. P. A.*, **1898**, 745.
[2] *J. Soc. Chem. Ind.*, **1885**, 611.
[3] *Ibid.*, **1894**, 1093.
[4] *Ibid.*, **1900**, 933.

Kippenberger[1] liberates the combined iodine by means of chromic acid and extracts the free iodine with chloroform and titrates with sodium thiosulphate solution.

Ditz and Margosches[2] proposes to modify Barrie's method by using potassium iodate as the oxidizing agent with either dilute hydrochloric or sulphuric acid, $KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$, and extracting the free iodine with toluene.

The method used by the writer is as follows: Five cc. of the tincture are placed in a separatory funnel together with 15 cc. dilute sulphuric acid and 30 cubic centimeters decinormal potassium dichromate. Let stand about ten minutes and then add to the mixture 20 cc. carbon tetrachloride. Shake thoroughly, and when the liquids have separated draw off the carbon tetrachloride solution of iodine. Repeat the shaking out three times with successive portions of 10 cc. each of carbon tetrachloride; titrate the combined solutions of iodine with decinormal thiosulphate. From the amount of total iodine thus determined deduct the free iodine and combined iodine as potassium iodide; the difference will be the amount of iodine existing as either ethyl or hydrogen iodide.

Alcohol.—In determining the alcohol in tincture of iodine it becomes necessary to convert the iodine into a non-volatile iodide before distillation.

Alcock[3] recommends the shaking of a convenient quantity of the tincture with mercury, until complete inversion of iodine, and then adding a small quantity of sodium or potassium hydroxide to prevent contamination of the distillate with traces of mercuric iodide.

Cameron[4] states when the iodine is fixed with potash it often causes "bumping" and recommends the use of iron turnings.

Roscoe and Schorlemmer[5] states when iodine is brought in contact with water and filings of iron or zinc colorless solutions of the respective iodides are formed.

Practically all the methods mentioned are unsatisfactory; in combining with the metals too much time is necessary and in most cases a small amount of volatile iodide is formed, and in using sodium or potassium hydroxide iodoform is formed.

Of the different methods investigated Alcock's proved the most satisfactory.

[1] *Analyst*, **1903**, 256.
[2] *J. Soc. Chem. Ind.*, **1905**, 45.
[3] *Proc. A. P. A.*, **1904**, 583.
[4] *Analyst*, **1902**, 87
[5] "Treatise on Chemistry," Vol. 1, p. 157.

ON THE DETERMINATION OF POTASSIUM BY THE COBALTI-NITRITE METHOD.[1]

By L. T. Bowser.

Received July 6, 1909.

Probably the first to make use of the reaction between sodium cobalti-nitrite and potassium as a test for the latter was DeKoninck, and this reagent is often called by his name. He utilized it only for qualitative purposes, however, and Adie and Wood[2] seem to have been the next to investigate its use. Various other brief statements concerning the reaction are to be found, and for convenience are noted here.[3] Crookes[4] says: "L. L. DeKoninck finds that if a 10 per cent. solution of sodium nitrite is mixed with cobalt chloride and acetic acid, the liquid forms are agents for the detection of potassium much more sensitive than platinum chloride. An immediate yellow precipitate is obtained in a solution containing one part KCl in 100 parts of water. It is still perceptible if diluted to 1/1000, but in the proportion of 1/2000 a precipitate is no longer obtained. Ammonia gives a similar but much less delicate reaction—sodium, magnesium, calcium, barium, strontium, iron, aluminium, and zinc salts are not precipitated by this reagent." Fresenius[5] says in part: "This freshly prepared reagent produces a yellow crystalline precipitate of potassium cobalti-nitrite, $K_3Co(NO_2)_6$.[6] In concentrated solutions this takes place immediately, but in more dilute ones only after some time. Ammonium salts give a similar reaction, but only in concentrated solutions." Substantially the same is given by Prescott and Johnson,[7] and they also assign for the formula, $K_3Co(NO_2)_6$. They remark that it is sparingly soluble in water, insoluble in alcohol and in a solution of potassium salts. Autenreith[8] determines potassium in silicates by precipitating it as the cobalti-nitrite after decomposing the silicate by HF and H_2SO_4 and removing the heavy metals. He allows the precipitate to stand 24 hours, then filters and brings into solution and determines as chloroplatinate or perchlorate.

The Method of Adie and Wood.—The only articles, however, in which there is described the full estimation of potassium by this method are the ones by Adie and Wood, and by Drushel. The procedure of Adie and Wood is to add 10 cc. of reagent and 1 cc. of strong acetic acid to 10 cc. of potash solution, allowing to stand over night, filtering the precipitate on a Gooch and washing with 10 per cent. acetic acid. The cobalt is precipitated by boiling with 2 or 3 cc. of a 10 per cent. solution of NaOH, the filtered solution made up to 100 cc., and aliquots of 20 cc. are taken for titration with $KMnO_4$. The solution is slowly acidified and $KMnO_4$ added until the pink color holds for a minute. According to this procedure 1 cc. of strictly $N/10$ $KMnO_4$ is equal to 0.0007858 gram K_2O. The authors find that the formula of the precipitate is $K_2NaCo(NO_2)_6.H_2O$. Some confusion seems to have occurred by reason of the similarity of this salt to tri-potassium cobalti-nitrite, as before noted, and the formula given by Fresenius and by Prescott and Johnson should be that just given. Sutton lays particular emphasis on the necessity of having a concentration of solution such that from 0.5 to 1.0 per cent. of K_2O is present, and finds that in too dilute solutions the precipitate runs through the filter.

Drushel's Method.—The method according to Drushel[1] is as follows: The potassium is precipitated as di-potassium-sodium-cobalti-nitrite by an excess of sodium cobalti-nitrite, the mixture evaporated on the steam bath, the precipitate filtered on asbestos and oxidized by hot standard $KMnO_4$. The excess of permanganate is bleached by an excess of standard oxalic acid, and the solution then titrated back to color with permanganate. One cc. of $N/10$ $KMnO_4$ is equal to 0.0008573 gram K_2O by this method. In making the titration a measured excess of $KMnO_4$ is diluted to ten times its volume and heated nearly to boiling, and the precipitate and asbestos are thrown in and stirred up. After 5 to 8 minutes manganese hydroxide separates out, when 5–25 cc. H_2SO_4 (1 : 7) are added, the solution stirred and allowed to stand a few minutes, after which the titration is completed.

Reactions Involved.—The method used for the preparation of the reagent is as follows: 220 grams sodium nitrite are dissolved in 400 cc. of water, 113

[1] Author's Note.—I had begun the study of this method before noticing the first of Mr. Drushel's papers, and thought it proper to carry on the investigation to a greater length than the latter. Although my general procedure chances to be very similar to his, the work has been influenced very little by his published results, and was made with a view of providing an adequate basis for future work, as well as of giving a review of the scattered literature on the subject. —L. T. B.

[2] *Jour. Chem. Soc.*, **77**, 1076. Sutton, "Volumetric Analysis," 9th Ed., pp. 61–3.

[3] Erdmann, *J. pr. Ch.* [1], **97**, 385 (1866); Sadtler, *Am. J. Sci.* [ii], **49**, 189 (1870); *Rev. of Am. Chem. Res.*, **1899**, 18.

[4] "Select Methods in Chemical Analysis," p. 1.

[5] "Qualitative Analysis" (Wells), 16th Ed., p. 133.

[6] This is evidently a mistake, and will be referred to later.

[7] "Qualitative Chemical Analysis," 6th Ed., p. 224.

[8] Freiburg i/B. Chem. Univ. Lab., *Centr. Min. Geol.*, **1908**, 513–17. Abstract in *Chem. Abs.*, **2**, 3038 (1908).

[1] *Am. Jour. Sci.*, **24**, 433–8 (1907); *Ibid.*, **26**, 329–32 (1908); *Ibid.*, **26**, 555–62 (1908).

grams cobalt acetate dissolved in 300 cc. of water and 100 cc. glacial acetic acid added. The solutions are poured together, mixed and gently warmed, NO_2 is evolved and evacuated by means of a filter pump kept running over night. The solution is then filtered and made up to a liter, when the reagent is ready for use. In the course of preparation the following reaction occurs, $21Co(C_2H_3O_2)_2.4H_2O + 14NaNO_2 + 4H(C_2H_3O_2) = Na_6Co_2(NO_2)_{12}.H_2O + 8Na(C_2H_3O_2) + 2NO + 6H_2O$, thus giving for its products sodium cobalti-nitrite, sodium acetate, and nitric oxide, which on contact with the air immediately becomes nitrogen peroxide. Similar results follow when the reagent is prepared from cobalt chloride or nitrate. From this equation it may readily be calculated that the ratio of sodium nitrite to cobalt acetate is 220 to 113, the grams per liter given by Adie and Wood. This gives about the maximum strength to which the solution may be made, since both salts are dissolved to about the saturation point. One cc. of this reagent contains 0.1886 gram of sodium cobalti-nitrite, which is equal to 0.0426 gram of K_2O. As will be shown later, however, it is actually necessary to use more than this amount of reagent in order to precipitate all the potash in condition suitable for work.

The reaction with a potassium salt in solution is: $Na_6Co_2(NO_2)_{12}.H_2O + 2K_2SO_4 = 2K_2NaCo(NO_2)_6.H_2O + 2Na_2SO_4$. The yellow precipitate, dipotassium-sodium-cobalti-nitrite, is very stable, as has been shown by Hofman and Burger[1] to be the case with a number of other cobalti-nitrites of similar nature, and has been found to be practically insoluble in water. When boiled with NaOH, as in the method of Adie and Wood, $Co(OH)_2$ is precipitated, while the filtrate contains a mixture of sodium and potassium nitrites. The reaction involved in titration with permanganate then becomes: $10KNO_2 + 20NaNO_2 + 6K_2Mn_2O_8 + 33H_2SO_4 = 11K_2SO_4 + 10Na_2SO_4 + 12MnSO_4 + 30HNO_3 + 18H_2O$. Hence $K_2Mn_2O_8 = 5/6K_2O$, from which 1 cc. $N/10$ $KMnO_4$ = 0.0007858 gram K_2O.

When the precipitate is treated directly with permanganate a different and somewhat more complicated reaction occurs. Trivalent cobalt is reduced to bivalent, and in so doing releases one atom of oxygen, which thereupon oxidizes an equivalent amount of the precipitate, thus reducing the amount of permanganate used. The final reaction is in effect: $10(K_2NaCo(NO_2)_6.H_2O) + 11K_2Mn_2O_8 + 58H_2SO_4 = 21K_2SO_4 + 5Na_2SO_4 + 10CoSO_4 + 22MnSO_4 + 60HNO_3 + 38H_2O$. Hence in this case $11K_2Mn_2O_8 = 10K_2O$ and $K_2Mn_2O_8 = 10/11 K_2O$, from which 1 cc. $N/10$ $KMnO_4$ = 0.0008573 gram K_2O.

Advantages of the Method.—There is a decided similarity between several of the insoluble potassium salts, in particular the platinichloride, the phosphomolybdate, and the cobalti-nitrite. Each is of a peculiar yellow color, and each is found to be best obtained for quantitative purposes by evaporation on the steam bath. One of the great advantages in the determination of potassium by the platinum method is the high molecular weight of the resulting precipitate, 485.8, giving a factor of 0.1941 for K_2O, which thus reduces to a very small amount any danger from minor errors of manipulation. The molecular weight of $K_2NaCo(NO_2)_6.H_2O$ is 454.61, and the factor for K_2O is 0.2074, thus giving to the determination the same advantage as that by the platinum method. In the opinion of the writer the gravimetric cobalti-nitrite method when properly conducted will be found nearly as accurate for most purposes as the older platinum method. Moreover, it presents a very decided advantage over the latter from the fact that by its aid potassium may be determined with equal accuracy whether it be present as chloride, sulphate or nitrate, and does not vary greatly from the truth when in the form of bicarbonate, chlorate or dibromate. Another of its advantages over the platinum method is the fact that the cost of reagent is very low, about one per cent. per determination.

Investigation of Adie and Wood's Method.—The method of Adie and Wood having given unexpectedly irregular results, a carefully planned and executed series of determinations was made in the hope of ascertaining the factors contributing to this irregularity. Most of the difficulty was found to be due to the method of precipitation, although the titration gave some trouble also. Three solutions were made up, containing 5 grams respectively of KCl, KNO_3, and K_2SO_4 per 500 cc., thus giving about the concentration recommended by Adie and Wood. One cc. then contained 0.00632 gram of K_2O as KCl, 0.004659 gram as KNO_3, or 0.005408 gram as K_2SO_4. All of the work noted in this paper was conducted upon C. P. salts, for while a method which works well on pure salts may or may not do so with complex substances,

[1] Roy. Acad. Sci. Munich, *Ber.*, **40**, 3298–3301. Abstract in *Chem Abs.*, **1**, 2542 (1907).

yet one which will not give good results under such conditions certainly cannot be depended upon for more difficult combinations.

Part of the following determinations were made by the method of Adie and Wood in full; they will be found under the heading "Alkali Method," from the use of NaOH to decompose the cobaltinitrite precipitate. The remaining ones were run by what is designated as the "Acid method," and were conducted identically like those by the alkali method until the potash precipitate had been filtered. The precipitate was then rinsed into a beaker with 25-50 cc. of water, the asbestos being left with it, a measured excess of $KMnO_4$ added, then 5 cc. of 1 : 1 H_2SO_4, and the mixture brought to boiling, accompanied by vigorous stirring. When all the precipitate had been decomposed the excess of $KMnO_4$ was bleached with $N/10$ oxalic acid. The amount of potash was obtained by multiplying the cc. of $KMnO_4$ used by the factor 0.0007858 previously derived. In Table I is given the result of a number of determinations, showing the volume of $KMnO_4$ consumed per 0.05 gram K_2O, the per cent. of potash found, and the percentage of deviation from the real results.

TABLE I.

Salt used.	No of dets.		$KMnO_4$. Alkali method.	$KMnO_4$. Acid method.	Per cent. K_2O. Alkali method.	Per cent. K_2O. Acid method.	Per cent. dev. Alkali method.	Per cent. dev. Acid method.
KCl	4	Max.	68.38		108.18		+ 8.18	
		Min.	67.64		106.30		+ 6.3	
		Ave.	68.03		106.90		+ 6.90	
	6	Max.		63.45		99.72		—0.28
		Min.		61.78		97.10		—2.90
		Ave.		62.20		97.76		—2.24
KNO_3	3	Max.	67.07		105.4		+ 5.40	
		Min.	62.52		98.26		— 0.78	
		Ave.	64.57		101.46		+ 1.46	
	6	Max.		64.61		101.54		+1.54
		Min.		61.17		96.14		—3.86
		Ave.		62.56		98.36		—1.64
K_2SO_4	6	Max.	70.35		110.56		+10.56	
		Min.	55.25		86.84		—13.16	
		Ave.	64.32		101.09		+ 1.09	
	7	Max.		63.52		99.82		—0.18
		Min		60.42		90.46		—5.04
		Ave.		62.29		97.92		—2.08
General average			65.52	62.36	102.98	98 02	2.98	1.98

It will be noted that the percentage found by the acid method is lower than that by the alkali, probably owing to the occurrence of a slightly different reaction, also that the average deviation is one per cent. less. The irregularities are entirely too great to permit the use of either method for quantitative purposes. The conditions were exactly the same for both methods, and all the precipitates were allowed to stand 14 hours before filtering. The acid method having been found superior in point of accuracy was used in the subsequent determinations; hence the results shown in Tables II and III are not as unfavorable to the method as they would have been had the original one been followed strictly.

It having thus been shown that, notwithstanding the exercise of the utmost care, considerable irregularities occur in the use of the original method of Adie and Wood, it remained to ascertain what factors might contribute to this end. In Table II is shown the effect of dilution of the potash solution, in this case KCl, upon the amount of potash found.

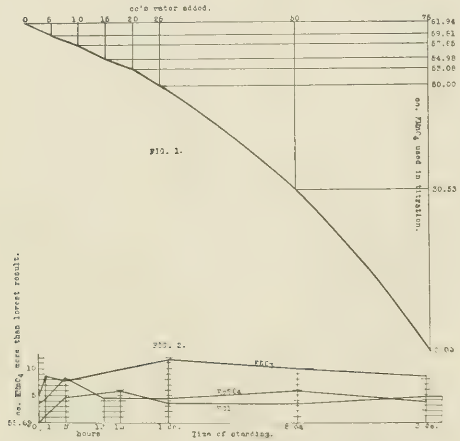
TABLE II.

No.	Cc. H_2O added.	Cc. $KMnO_4$	Per cent. K_2O found.
1	0	61.94	97.34
2	5	59.81	94.00
3	10	57.85	90.92
4	15	54.98	86.40
5	20	53.08	83.42
6	25	50.00	78.58
7	50	30.53	47 98

Fig. 1, based on the results set forth in this table, shows graphically the consequence of dilution, the volume of $KMnO_4$ used in the titration of the potash precipitate from a solution of ordinary concentration being taken as the basis of comparison. The curve shows that with minor variations the volume of $KMnO_4$ consumed, and consequently the percentage of potash recovered, varies inversely with the dilution. A continuation of the curve to the line of 0 cc. $KMnO_4$ shows that with about 75 cc. of water added to the original solution there would be no precipitation. This dilution would give one part K_2O in 1600 as the point at which precipitation would not occur, thus agreeing closely with the previously noted statement of De Koninck. It is quite noticeable that the solutions so dilute are very slow in giving up their potash to the reagent, the precipitate is finer in grain, and the supernatant solution is darker in color. Moreover, with increasing dilution there is greater difficulty in detaching the precipitate from the sides of the beaker and in the case of the very dilute ones it was impossible to remove it all. Sutton attributes the irregularities of the results with solutions more dilute than 0.5 per cent. K_2O to a tendency of the precipitate run through the filter. In order to test the point the filtrates from this dilution series were concentrated and allowed to stand for some

time, then filtered. In every case the results showed practically a blank, hence it is evident that this explanation does not satisfactorily account for the case. The conclusion is forced upon us that such dilution prevents the formation of the precipitate or perhaps decomposes the reagent as fast as added. This matter is a serious one, for in the case of the most determinations it is impracticable if not impossible to bring the dilution within such limits as necessary.

Another possible cause of irregularity was the length of time allowed before filtration of the precipitate, and accordingly the series shown in Fig. 2 was undertaken to find if this did contribute in any way to the observed variations.



It will be seen that while variations from this cause are not of the magnitude of those occasioned by dilution, they are yet serious enough to cause a very undesirable amount of irregularity. The curves are all based upon the lowest titration result and show that in general the initial result is the lowest, that it rises quickly the first few hours, and gradually settles to a fairly constant quantity. The reagents and asbestos were tested in blank, but no permanganate was consumed for either. No further investigations were conducted on the Adie and Wood method, except a series which will be noted later to determine the effect of other metals present. The results just presented are sufficient to condemn the practice of precipitation by standing for almost all purposes, since it gives very uncertain results at best; the potash found varies inversely with the concentration, and the time of standing exercises considerable influence on it.

Variations Tried.—Having thus found that the method of Adie and Wood was inapplicable to ordinary work, my attention was next directed to the finding of some suitable modification that would be reliable. It was evident that most of the difficulty encountered in the use of my "acid method" lay in the manner of precipitation of the potash, although some slight error was introduced by the method of titration. After several trials of various methods I found, like Drushel, that the most satisfactory way of conducting the precipitation, and of eliminating the errors attributable to dilution and time of standing, was that of evaporating together the potash solution and reagent to pastiness on the steam bath, taking up with water and filtering through a Gooch asbestos filter. Some of the titrations were made like those of the preceding "acid method," but later it was found expedient to defer adding sulphuric acid until after boiling the mixture. It has been found convenient to filter the precipitate on the form of filter devised by Shimer,[1] using asbestos for the pad. In no case has any difficulty been experienced in removing the precipitate from the sides of the glass tube, as was noted by Drushel with crucibles. The filter plate should be taken out and rinsed off to avoid the danger of its becoming coated with manganese hydroxide.

Addition of Acetic Acid in Precipitating.—It was found by a series of tests that the presence or absence in precipitating of 1 cc. of strong acetic acid made no apparent difference in the titration results, yet its addition should not be neglected, as without it the precipitate clings tenaciously to the dish. A scheme for titrating the filtrate instead of the precipitate was found unavailing. The time consumed in titrating was found to be approximately one-sixth of that required by Drushel's method.

Procedure Adopted.—My modification of the method of Adie and Wood is as follows: The potash is brought into solution by any desired means, any excess of acid is driven off by evaporation, the residue taken up with water and any interfering metals removed by boiling with sodium carbonate, the solution filtered and the precipitate washed with hot water. Filtrate and washings are concentrated, acidified with acetic acid, and the K_2O precipitated as presently described.

[1] *Jour. Am. Chem. Soc.*, **27**, 287 (1905).

For all the work of this section solutions of various potassium salts were made up having a strength of 0.75 per cent., or 1 cc. contains 0.0075 gram K_2O. In each determination 5 cc. were taken, making a total of 0.0375 gram K_2O. By theory this amount should require 43.74 cc. $KMnO_4$, making the volume of permanganate solution used about as large as possible and thus reducing the effect of titration errors. A quantity of potash solution equivalent to 0.0375 gram K_2O is placed in a porcelain evaporating dish, 10 cc. reagent added, and then 1 cc. strong acetic acid. The mixture is evaporated to pastiness on the steam bath, and after cooling is stirred up with 25–50 cc. water and filtered on asbestos, washing with sufficient water to remove the excess of reagent. The precipitate and felt are now transferred to a 250 cc. beaker, any adhering particles of the precipitate being removed from the sides of the tube by rubbing with a rubber tipped rod and rinsing into the beaker. An excess of permanganate is now added and the contents of the beaker brought to boiling. When they begin to darken, 5 cc. H_2SO_4 (1 : 1) is added and well agitated, then titration with $N/10$ oxalic acid and permanganate carried out to the usual end point. The cc. $KMnO_4$ used, multiplied by the factor 0.0008573, gives the grams K_2O.

Excess of Reagent.—It has been shown previously that 1 cc. of reagent is equal to 0.04 gram K_2O, hence 2 cc. would seem to be sufficient for all ordinary purposes. That such is not the case, however, is shown in Table III. These determinations were made on different days, one on KNO_3 and the other on KCl.

TABLE III.

No.	Cc. $KMnO_4$.	Per cent. K_2O	Cc reagent.	No.	Cc. $KMnO_4$	Per cent. K_2O.
1.......	17.9	40 8	1	6	3.75	8.57
2.......	29.4	67.2	2	7	6.70	15.32
			3	8	10.05	22.45
3.......	42.9	98.15	4			
4	43.95	100 55	5	9	22.15	50.65
5.......	44.07	100.75	10	10	43.55	99.57

The tabulated results show that while on some days practically all the potash will be precipitated by 5 cc. of reagent, yet at other times it will not; hence it is necessary to use 10 cc. reagent for each equivalent of 0.04 gram K_2O. Small volumes of the reagent precipitate the potassium in a state of division so fine as to render it impossible to filter without a great deal of running through. The filtrates from precipitations with 5.0 cc. or less of reagent are usually pink, as contrasted with the wine color of those containing a proper excess. In Table IV is shown the result of six determinations conducted exactly as described by Drushel.

TABLE IV

No.	Salt.	Cc. $KMnO_4$.	Wt. K_2O.	Diff K_2O.	Per cent. K_2O.	
1....	KNO_3	45 90	0.03933	+0.00183	104.9	
2 ...	K_2SO_4	46 10	0 03954	+0 00204	105 4	
3....	KNO_3	46 25	0 03965	+0 00215	105 75	
4....	KNO_3	45.45	0.03897	+0.00147	103 9	
5....	KNO_3	45.85	0.03931	+0.00181	104.8	
6....	KNO	45.25	0.03880	+0.00130	103.45	Ave. 104.7 per cent.

It will be seen that the results are higher than they should be, the average being 4.7 per cent. too much. The greatest of care was exercised with all these tests, and no reason is apparent for the high results.

Gravimetric Determination.—In Table V is given the results of six determinations on C. P. salts made by the gravimetric method, weighing the precipitate in carefully dried Gooches:

TABLE V.

No.	Wt. ppt.	Wt. K_2O.	Diff. K_2O.	Per cent. K_2O	
1......	0.1835	0.03805	+0.00055	101.5	
2......	0.1834	0.03804	+0.00054	101 5	
3......	0.1825	0.03786	+0.00036	101.0	
4	0.1844	0.03827	+0.00077	102 05	
5......	0.1823	0.03782	+0 00032	100 85	
6......	0.1802	0.03738	—0.00012	99 68	Ave. 101 09 per cent.

The average, 101.09 per cent., is seen to be a trifle higher than that found by the volumetric method, and this would seem to indicate that perhaps there is some secondary reaction occurring that exercises an influence on the composition of the precipitate, which is assumed to be $K_2NaCo(NO_2)_6.H_2O$, as given by Adie and Wood. Some of the minor variations were probably due to exterior conditions, but as the amount of reagent at hand was getting rather limited the series was not repeated.

Results from My Method.—In order to furnish a reliable basis for comparing the amounts of potash found with those actually taken, the series of determinations tabulated in Table VI was made rather extended.

TABLE VI.

Salt used.	No. of deters.		Cc. $KMnO_4$.	Wt. K_2O.	Diff. K_2O.	Per cent K_2O.
KCl	10	Max.......	45.20	0.03876	+0 00126	103.30
		Min.......	43.35	0 03734	—0.00016	99.57
		Ave.......	44 05	0.03777	+0.00027	100.70
KNO_3	10	Max.......	44.65	0.03828	+0.00078	102.10
		Min	43.35	0.03717	—0 00033	99.12
		Ave.......	43.95	0.03768	+0.00018	100.50
K_2SO_4	8	Max.......	44.60	0.03828	+0.00078	102.10
		Min.......	43.85	0.03760	+0.00010	100.30
		Ave.......	44.20	0.03789	+0.00039	100.90

It will be seen that the amount of deviation between different determinations is much greater

in the volumetric method than in the gravimetric, the cause probably being in the titration with $KMnO_4$. It will be found on working over the last five results of Drushel's Table I, that the amount of K_2O found is 109.30, 108.00, 107.10, 105.85, and 107.65 per cent. of that taken, while with the first five of his Table II they run 100.40, 102.10, 100.00, 99.37, and 104.20 per cent. of the amount used. It is interesting to note that the average of these ten determinations is 104.40 per cent., as compared with the 104.7 per cent. I obtained in Table V. This would seem to show quite plainly that there is something in the method of titration that gives the difficulty with his method even more than with mine. The method of precipitation as now practiced seems to need but little further attention save as to the removal of interfering substances.

Radicle Combined with K_2O.—Practically no difference is to be noticed in the accuracy of the determinations whether the acid radicle be Cl, NO_3, or SO_4, and this point is worthy of particular emphasis in view of the very decided saving of time, labor, and accuracy possible when it is not necessary to convert the potassium to the chloride form. The results obtained in the determination of potassium combined with various other acid radicles are shown in Table VII:

TABLE VII.

No.	Salt.	Cc. $KMnO_4$.	Wt. K_2O.	Diff. K_2O.	Per cent. K_2O.	Ave. per cent.
1	$KClO_3$...........	44.85	0.03846	+0.00096	102.50	
2	$KClO_3$...........	45.50	0.03901	+0.00151	104.00	
3	$KClO_3$...........	45.15	0.03871	+0.00121	103.25	
4	$KClO_3$...........	44.25	0.03794	+0.00044	101.15	102.70
5	K_2CrO_4..........	43.45	0.03725	−0.00025	99.35	
6	K_2CrO_4..........	42.30	0.03627	−0.00123	96.72	98.05
7	$K_2Cr_2O_7$.........	43.30	0.03713	−0.00037	99.00	
8	$K_2Cr_2O_7$.........	44.35	0.03803	+0.00053	101.40	100.20
9	K_2CO_3...........	40.25	0.03451	−0.00299	92.03	
10	K_2CO_3...........	39.40	0.03378	−0.00372	90.08	
11	K_2CO_3...........	38.80	0.03327	−0.00423	88.71	
12	K_2CO_3...........	39.50	0.03387	−0.00363	90.31	90.28
13	$KHCO_3$..........	45.50	0.03862	+0.00112	103.00	
14	$KHCO_3$..........	44.60	0.03828	+0.00078	102.10	
15	$KHCO_3$..........	44.90	0.03850	+0.00100	102.70	102.60
16	$K_4Fe(CN)_6$.......	43.75	0.03751	±0.00001	100.00	
17	$K_4Fe(CN)_6$.......	..	....	....	....	
18	$K_3Fe(CN)_6$.......	...	.....	....	....	
19	$K_3Fe(CN)_6$.......	44.50	0.03820	+0.00070	101.85	

The chlorate gives results somewhat higher than the true ones, the chromate about as much lower. The dichromate seems to give quite reliable results, as is also the case with the ferro- and ferricyanide. With the last two, however, it is not always possible to get an accurate end point, since it is apt to be obscured by a dark color in the solution, whence the two blanks noted. Potash may also be estimated with fair accuracy in the form of bicarbonate, but strangely enough not as carbonate. The results show that the method is directly applicable to almost any salt of potassium except the carbonate.

Interfering Substances.—It having been found that the method is applicable with a fair degree of accuracy to the estimation of potassium combined with various acid radicles, it remained to investigate the influence on the determination of various

TABLE VIII.

No.	Foreign salt.	Radicle.	Wt. radicle.	Cc. $KMnO_4$.	Wt. K_2O.	Diff. K_2O.	Per cent. K_2O.
1	Na_2HPO_4	P_2O_5	0.5	14.40	0.01235	−0.02515	32.92
2	Na_2HPO_4	P_2O_5	0.1	40.45	0.03469	−0.00281	92.48
3	Na_2HPO_4	P_2O_5	0.05	43.90	0.03764	+0.00014	100.40
4	Na_2HPO_4	P_2O_5	0.01	44.10	0.03781	+0.00031	100.80
5	$Na_2B_4O_7$	B_2O_3	2.5	0.15	0.00013	−0.03737	0.34
6	$Na_2B_4O_7$	B_2O_3	0.125	41.10	0.03524	−0.00226	93.97
7	$Na_2B_4O_7$	B_2O_3	0.05	28.00	0.02401	−0.01349	64.02
8	SiO_2	SiO_2	1.0	44.90	0.03850	+0.00100	102.70
9	Na_2SiO_3	SiO_2	1.0	9.30	0.00797	−0.02953	21.16
10	$BaCl_2$	BaO	1.0	14.00	0.01200	−0.02550	32.01
11	$BaCl_2$	BaO	0.1	45.60	0.03910	+0.00160	104.30
12	$BaCl_2$	BaO	0.01	44.90	0.03850	+0.00100	102.70
13	$MnSO_4$	MnO	0.5	27.60	0.02366	−0.01384	63.11
14	$MnSO_4$	MnO	0.05	44.50	0.03815	+0.00065	101.75
15	$Al_2(SO_4)_3$	Al_2O_3	0.3125	1.05	0.00090	−0.03660	2.40
16	$Al_2(SO_4)_3$	Al_2O_3	0.0625	40.50	0.03472	−0.00278	92.60
17	$Al_2(SO_4)_3$	Al_2O_3	0.03125	44.50	0.03815	+0.00065	101.75
18	$CuSO_4$	CuO	0.25	33.50	0.02872	−0.00878	76.59
19	$CuSO_4$	CuO	0.05	45.40	0.03893	+0.00143	103.80
20	$CuSO_4$	CuO	0.05	41.40	0.03516	−0.00234	93.74
21	$MgSO_4$	MgO	1.00	26.70	0.02289	−0.01461	61.05
22	$MgSO_4$	MgO	0.10	44.30	0.03798	+0.00048	101.30
23	$MgCl_2$	MgO	0.50	32.45	0.02782	−0.00968	74.19
24	$MgCl_2$	MgO	0.05	24.05	0.01969	−0.01781	52.51
25	$CaSO_4$	CaO	0.1629	43.15	0.03700	−0.00050	98.66
26	$CaCl_2$	CaO	1.00	39.70	0.03404	−0.00246	90.77
27	$CaCl_2$	CaO	0.5	41.00	0.03515	−0.00235	93.74
28	$CaCl_2$	CaO	0.01	39.15	0.03357	−0.00393	89.51
29	$CaCl_2$	CaO	0.1	18.30	0.01569	−0.01181	41.84
30	$CaCl_2$	CaO	0.03	27.95	0.02396	−0.01345	63.90
31	$CaCl_2$	CaO	0.01	32.45	0.02782	−0.00968	74.19
32	$Ca(NO_3)_2$	CaO	1.0	25.95	0.02285	−0.01425	59.33
33	$Ca(NO_3)_2$	CaO	0.50	0.45	0.00044	−0.03706	1.48
34	$Ca(NO_3)_2$	CaO	0.10	38.75	0.03322	−0.00428	88.60
35	$Ca(NO_3)_2$	CaO	0.10	28.30	0.02426	−0.01224	64.71
36	$Ca(NO_3)_2$	CaO	0.05	40.85	0.03502	−0.00148	93.40
37	$Ca(NO_3)_2$	CaO	0.01	32.80	0.02812	−0.00938	74.99
38	$Ca(NO_3)_2$	CaO	0.01	39.70	0.03404	−0.00346	90.77
39	$Fe(NO_3)_3$	FeO	1.0	7.05	0.00604	−0.03146	16.12
40	$Fe(NO_3)_3$	FeO	0.5	9.65	0.00827	−0.02923	22.06
41	$Fe(NO_3)_3$	FeO	0.2	30.45	0.02611	−0.01039	69.62
42	$Fe(NO_3)_3$	FeO	0.1	43.80	0.03755	+0.00005	100.15
43	$Fe(NO_3)_3$	FeO	0.05	40.75	0.03494	−0.00256	93.17
44	$Fe(NO_3)_3$	FeO	0.04	16.05	0.01376	−0.02374	36.70
45	$Fe(NO_3)_3$	FeO	0.01	38.40	0.03292	−0.00458	87.80
46	$Fe(NO_3)_3$	FeO	0.005	40.65	0.03485	−0.00265	92.94
47	$FeCl_3$	FeO	1.0	2.00	0.00171	−0.03578	4.57
48	$FeCl_3$	FeO	0.5	9.00	0.00772	−0.02978	20.58
49	$FeCl_3$	FeO	0.2	35.45	0.03040	−0.00710	81.05
50	$FeCl_3$	FeO	0.1	44.55	0.03820	+0.00070	101.90
51	$FeCl_3$	FeO	0.5	43.80	0.03755	+0.00005	100.15
52	$FeCl_3$	FeO	0.04	17.55	0.01505	−0.02245	40.13
53	$FeCl_3$	FeO	0.01	41.85	0.03588	−0.00162	95.68
54	$FeCl_3$	FeO	0.005	41.40	0.03549	−0.00201	94.66

other substances, evidently a point of vital importance to the value of the method as applied to actual work. All the substances most likely to occur in ordinary samples have been included in this investigation. It has been previously noted that De Koninck says the ordinary metals do not give a precipitate with this reagent. This was found to be true, but nevertheless they may under many conditions work serious harm to the determination. When subjected to the beaker method of precipitation they seem to influence the results but little, but in the evaporation method radically different conditions occur, in consequence of which there are probably reactions between these metals and the potash precipitate which produces great irregularity. My results on this investigation are given in Table VIII.

But little comment is needed on the results given here. They show that in general a small amount of a foreign metal may give results a little high, but a large amount tends to materially reduce the amount of potash recovered. The greatest danger would seem to exist in the case of $MgCl_2$, the iron and the soluble calcium salts. Evidently it is unsafe to trust a determination where any of these metals are present. Adie and Wood advised precipitating out all these interfering metals by boiling with Na_2CO_3, and this would seem to be the best procedure.

Irregularity of Results.—Drushel has given a short series of results where metals are present of which brief mention seems appropriate. He seems to have had $CaCl_2$ and $MgCl_2$ present in each test, while $BaCl_2$ and $Sr(NO_3)_2$ were added in some cases. From the results it seems almost impossible that these could have been subjected to his adopted mode of precipitation in view of what I have found in the preceding determinations. In Table IX is given a comparison of three of his results and three of mine run by the beaker method of precipitation of Adie and Wood:

TABLE IX.

Drushel's.

No.	Wt. $CaCl_2$.	Wt. $MgCl_2$.	Wt. $BaCl_2$.	Gram K_2O taken.	Gram K_2O found.	Gram error.	Per cent. K_2O.
2	0.3	0.5	...	0.0237	0.0234	—0.0003	98.74
7	0.5	1.0	...	0.0711	0.0713	+0.0002	100.27
6	0.5	1.0	0.5	0.0237	0.0251	+0.0014	105.90

Mine.

No.	Wt. salt.	Gram K_2O taken.	Gram. K_2O found.	Error.	Per cent. K_2O.
1 $Ca(NO_3)_2$....	0.1984	0.0315	0.03111	—0.00039	98.76
2 $MgSO_4$.......	0.1986	0.0315	0.03033	—0.00017	96.29
3 $BaCl_2$........	0.2330	0.0315	0.03579	+0.00429	113.60

It is worthy of note that there is a general agreement between the two series, and it would seem from this that perhaps his precipitations may have been made by this latter method. The very fact that $MgCl_2$ was present in every case would seem evidence enough that this precipitation was not made by evaporation, since this would have unavoidably liberated enough HCl to seriously affect the results. It should be plainly understood in a consideration of these results that it is very unlikely any two workers will be able to obtain the same results with these substances present, for in almost every case extreme irregularity characterizes the determinations thus made. The same general conclusion would surely result however, that small amounts do not matter greatly, but that larger ones must not be present. The one conspicuous and fortunate exception is sodium. From the fact that this is present in the constitution of the precipitate it might be inferred that it would cause no interference, and numerous tests with even very large amounts show this to be the case.

Precautions Necessary.—To insure success in the use of the method the following precautions must be observed. Ammoniacal fumes should be absent. Should reagents or asbestos be of doubtful quality blanks must be run on them and a correction made on the regular results. The potash solution should not be too dilute previous to precipitation. Do not neglect the addition of strong acetic acid, and should difficulty be experienced at any time with sticking of the precipitate to the sides of the dishes it will be found well to add a somewhat larger amount. Do not allow evaporation to proceed too far as it may in some cases cause trouble. Care should be exercised in evaporating to see that too vigorous a heat is not applied, since when the solution is getting thick it may spirt out of the dish if too hot. In carrying out the titration it is a matter of common occurrence to have manganese hydroxide stick to the sides of the beaker. This must be taken up by a slight excess of oxalic acid, assisted if need be by loosening by a rubber-tipped rod. When all the coating has disappeared the rod should be taken out and rinsed, since rubber would affect the permanganate titration.

Conclusion.—This method seems to be one of great promise and its development will be a matter of interest to all chemists, although to none in such a degree perhaps as with agricultural workers. In conclusion, I wish to acknowledge my

indebtedness to Mr. Drushel for the assistance his papers have been to me in the latter part of my work. He has done a great deal of praiseworthy work in connection with the method. A great deal of assistance has also been afforded by the articles previously mentioned. Since the preparation of this article, and too late to be discussed in it, the paper of Shedd[1] has appeared on the applicaiton of Drushel's method to the estimation of total potassium in soils.

OHIO AGRICULTURAL EXPERIMENT STATION,
WOOSTER, OHIO

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON EXTRACTS AND LEMON OILS.

By R. S. HILTNER.

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The method proposed by Chace[2] for determining citral in lemon oils and extracts has been adopted almost universally by food and drug chemists. It has afforded a valuable means of detecting spurious and adulterated products. Experience has shown that for accuracy the method leaves little to be desired. It is applicable, with slight modifications, to all grades of commercial extracts giving uniformly reliable results. Other methods have been proposed for the estimation of citral, but, according to Chace[3] and Gildemeister and Hoffman,[4] all have failed because of insufficient accuracy.

By the method to be described in the following paragraphs, the author has sought to eliminate certain difficulties encountered in the various other methods. The reagent used, although active with other aldehydes, is much more selective of citral than other reagents that have hitherto been suggested, and reacts negatively with aldehydes, other than citral, commonly present in commercial lemon extracts and oils. Its action, moreover, is quite independent of temperature and time. The proposed method is colorimetric in principle, making use of a dilute alcoholic solution of metaphenylene diamine hydrochloride as the reagent. This substance reacts quickly with citral at room temperature, yielding a clear, yellow-colored solution, the intensity of color being proportional to the amount of citral present. The color produced is reasonably permanent. The details of the method, as at present developed, are as follows:

REAGENTS.

Metaphenylene Diamine Hydrochloride Solution.—Prepare a 1 per cent. solution of metaphenylene diamine hydrochloride in 50 per cent. ethyl alcohol. Decolorize by shaking with fuller's earth, or animal charcoal, and filter. The solution should be bright and clear, free from suspended matter and practically colorless. It is well to prepare only enough solution for the day's work, as it darkens on standing. The color may be removed from old solutions by shaking again with fuller's earth or animal charcoal.

Standard Citral Solution.—Dissolve 0.250 gram of C. P. citral in 50 per cent. ethyl alcohol and make up the solution to 250 cc.

Alcohol.—For the analysis of lemon extracts, 90 to 95 per cent. alcohol should be used, but for terpeneless extracts alcohol of 50 to 60 per cent. strength is sufficient. Filter to remove any suspended matter. The alcohol need not be purified from aldehyde. If not colorless, render slightly alkaline with sodium hydroxide and distil.

APPARATUS.

Any convenient form of colorimeter may be used. The writer has obtained concordant and satisfactory results with the use of a form of colorimeter designed by Oswald Schreiner[1] and prefers this form. By lining the inner tubes with unglazed, opaque, black paper, so as to eliminate side lights, and leaving only the discs of light at the bottom of the tubes visible, much closer comparisons may be drawn. Good results were secured also with Eggertz tubes. With this latter apparatus alcohol is added, small quantities at a time, to the stronger colored solution until, after shaking and viewing transversely, the colors in the two tubes are exactly matched. Calculations are then made by establishing a proportion between the volume of samples taken and the final dilutions.

MANIPULATION.

All of the operations may be carried on at room temperature. When it is desired to determine citral by weight in the sample, weigh into a 50 cc. graduated flask, 25 grams of the extract and make up to the mark with alcohol (90 to 95 per cent.); stopper the flask and mix the contents thoroughly. Assuming the use of a Schreiner colorimeter, pipette into the colorimeter tube 2 cc. of the above solu-

[1] THIS JOURNAL, **1**, 302 (1909).

[2] *Jour. Amer. Chem. Soc.*, **28**, 1472 (1906).

[3] *Ibid.*, **28**, 1473 (1906).

[4] "The Volatile Oils," Gildemeister and Hoffman, trans. by Edw. Kremers.

[1] *Jour. Amer. Chem. Soc.*, **27**, 1192 (1905).

tion, add 10 cc. of metaphenylene diamine hydrochloride reagent and complete the volume to 50 cc. (or other standard volume) with alcohol. Compare, at once, the color with that of the standard, which should be prepared at the same time, using 2 cc. of standard citral solution and 10 cc. of the metaphenylene diamine reagent, and making up to the standard volume with alcohol. From the result of this first determination calculate the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample under examination, then repeat the determination. Make several readings, which should agree closely, and from the average, or the totals, calculate the amount of citral in the sample. In the case of samples colored with naphthol yellow S, or martius yellow, add a drop of concentrated hydrochloric acid to both sample and standard before adding the metaphenylene diamine reagent. Unless very strongly dyed, the effect of the coloring matter is inappreciable. When the amount of citral in the sample is small (less than 0.1 per cent.) it is well to take a larger aliquot portion of the sample, rather than to take a correspondingly smaller amount of the standard solution, in order to produce a strong yellow, necessary for accurate comparisons.

Citral in lemon oil may be determined with some degree of accuracy, in a similar manner, by first making an "extract." Five to eight grams in 100 cc. of alcohol is a convenient strength to use. The same difficulty obtains here, of course, as with the fuchsin-sulphurous acid method, namely, as stated by Chace that "the error made in comparing the solution and standard becomes so great when multiplied to correct for the dilution that it somewhat impairs the usefulness of the method for oils." However, it is safe to say that the results obtained are accurate within 0.2 or 0.3 per cent.

A number of experiments have shown that at room temperature the metaphenylene diamine hydrochloride reagent produces no color reaction with small amounts of acetaldehyde. It is therefore unnecessary to use aldehyde-free alcohol. The small quantity of acetaldehyde commonly present in rectified commercial alcohol is not visibly affected by the reagent. The maximum intensity of the color reaction with citral seems to be developed immediately and therefore observations may be made at once. The color normally is quite permanent and hence considerable latitude in time is allowable. Observations made immediately and again after half hour standing at room temperature gave practically the same results.

In the case of commercial terpeneless extracts, the yellow color develops to its full extent at once and holds without change for thirty minutes or more. The same is usually true of ordinary extracts containing lemon oil terpenes. Rarely, the yellow color at first produced gradually changes to a yellowish green tint. In this latter case, therefore, it is necessary to make the comparisons of color immediately after adding the reagents. In the course of the year's work in this laboratory, out of a large number of samples examined, only one sample of lemon oil and three of commercial lemon extracts (all purported to be pure products) gave this abnormal color, that is, a yellowish green tint instead of the characteristic yellow. In these four cases, and with the sample of citronellal mentioned below, the colors produced, which varied from yellowish green to greenish blue, are now believed to be due to the blending of the yellow tint from citral with the blue produced by the impurity common to all, probably partially oxidized limonene. This subject is being investigated. Obviously, the citral in such abnormal products cannot be accurately determined by the foregoing method. Quite recently, it was observed that when oil of lemon or oil of orange was allowed to stand exposed to the air for a few days, a greenish yellow color was produced on the addition of the metaphenylene diamine reagent and alcohol; the longer the exposure the darker and more bluish was the color yielded. From this it is inferred that in the few abnormal cases noted the lemon oil had become in part changed by oxidation. Apparently, the terpenes only undergo change, since no terpeneless extracts examined gave any abnormal color. It is obvious too from the foregoing, that alcohol in the extracts prevents the oxidation. Extracts that are properly made from pure fresh oil, direct from the coppers, conditions that usually obtain, may easily be examined for citral by this method.

Other normal constituents of lemon oil seem to be unaffected by metaphenylene diamine hydrochloride. Dilute solutions of citronellal in alcohol yield no color when treated with the reagent, except after standing at least thirty minutes. It was noted that slowly a slight blue or greenish tint developed. From recent experiments it is believed that this final color was due to impurities, terpenes probably, in the citronellal used. The

sample was labeled "pure citronellal." It was not tested further to determine its quality.

The effect of the reagent on limonene has not yet been fully determined. Most of the samples of lemon oil tested gave the normal yellow color that was permanent and identical with that produced with pure terpeneless citral solution and correct in intensity for the amount of citral present. Since limonene is present in lemon oil to the extent of about 90 per cent., it is therefore reasonable to infer that it does not react with metaphenylene diamine hydrochloride, or at least does not produce a distinctive color. However, the only sample of limonene obtainable, when dissolved in alcohol and tested with the reagent, produced a strong, clear, indigo-blue color. Here again partial oxidation may account for this abnormal color. The same result was obtained after redistilling the sample. This sample was procured from a very reliable firm and was labeled "pure limonene." It is interesting to note that under the same conditions, ordinary American turpentine, in dilute solution in alcohol, gives the same blue color.

The degree of accuracy of the method is indicated in Table I. Weighed amounts of pure citral were dissolved in 50 per cent. alcohol and tested by the process described. The tests were made under varying conditions of temperature and time of standing after addition of the reagent, using in some cases aldehyde-free alcohol and in others ordinary commercial "rectified spirit" as the diluent.

TABLE I.

	Gram citral per 100 cc.		
No.	Used.	Found.	Difference.
1	0.0800	0.0849	+0.0049
2	0.0666	0.0700	+0.0034
3	0.0500	0 0500	0.0000
4	0.1000	0.0990	—0.0010
5	0.0956	0.0946	—0.0010
6	0.0500	0.0500	0.0000
7	0.1200	0.1170	—0.0030
8	0.0610	0.0610	0.0000
9	0.2000	0.1970	—0.0030
10	0.0250	0.0243	—0 0007
11	0.0250	0.0246	—0.0004
12	0.2025	0.2044	+0.0019

Table II shows the results of tests of commercial extracts by Chace's method and by the one here proposed.

It is apparent in the following table that fuchsinsulphurous acid tends to give slightly higher values for citral than metaphenylene diamine. This is believed to be due to the positive reaction of the former reagent with acetaldehyde and citronellal which are probably always present in minute quantity in commercial extracts and which give no color reaction with the latter reagent. Sampes Nos. 5, 8 and 9 show slightly less citral by fuchsin than by the other reagent. The significance of this is not clear. It is at least possible that the discrepancy is due to experimental error.

TABLE II.

		Gram citral per 100 cc.	
No. of sample.	Kind of extract.	By fuchsin sulphurous acid.	By metaphenylene diamine hydrochloride.
1	Terpeneless	0.100	0.098
2	"	0.059	0.056
3	"	0.117	0.098
4	"	0.117	0.093
5	"	0.072	0.079
6	8.4 per cent. lemon oil	0.270	0.264
7	Terpeneless	0 074	0.064
8	Made from lemon oil and lemon grass oil, yellow dye	0.016	0.019
9	Terpeneless	0.045	0.053
10	5.25 per cent. lemon oil	0.326	0.252
11	Terpeneless with citral from lemon grass oil	0.313	0.305
12	Terpeneless	0.137	0.117
13	"	0.078	0.061
14	"	0.096	0.088
15	"	0.088	0.086

In order to ascertain how nearly uniform the results would be by different operators, the same samples of commercial extracts were submitted to three analysts in this laboratory. The results are given in Table III, expressed as percentage of citral.

TABLE III.

	Sample No.						
Analyst.	1.	2.	3.	4.	5.	6.	7.
A. E. Leach	...	0.060	0.102	0.032	0.388	...	...
F. H. Wise	0.097	0.060	0.100	0.030	...	0.098	0.080
R. S. Hiltner	0.098	0.056	0.098	0.040	0.344	0.093	0.079

In brief, the apparent advantages of the method are, first, that all operations may be carried on at room temperature and the tests may be made immediately after adding the reagent. Second, it is unnecessary to use especially purified alcohol, free from aldehyde. Third, more nearly correct results for citral may be secured in the analysis of commercial extracts, since the reagent used acts negatively with acetaldehyde and citronellal, usually present in small quantity in such products.

The author wishes to acknowledge his indebtedness to Mr. Albert E. Leach for his kind assistance and helpful suggestions in this work.

DENVER, COLO., July, 1909.

THE INFLUENCE OF SHADE UPON THE COMPOSITION OF PLANTS.

By R. W. Thatcher.

Received October 26, 1909.

About two years ago the writer, together with H. R. Watkins, published a brief note on the "Influence of Shade during Ripening upon the Proximate Constituents of the Wheat Kernel."[1]

The experiments there described have been amplified and extended to other crops than cereals. Different densities of shade, different lengths of time of shading, and various different crops have been employed. The same general methods of arranging the shade and of harvesting the crops were used as are recorded in the former paper. The methods of analysis employed were those of the Official Agricultural Chemists.

A large number of shaded *versus* unshaded samples have been analyzed. Some typical results are included in the accompanying table. Many others might be added, but would serve only to confirm the facts which are probably sufficiently illustrated by those which are presented.

Results of analysis.

				Composition of dry matter.					
Crop and variety.	Kind of shade.	Moisture.	Dry matter.	Ash.	Protein.	Fats.	Fiber.	Starch.	Undetermined.
Potatoes:									
Burbank	none	77.65	22.35	4.95	9.49	0.13	2.92	70.50	12.01
Burbank	burlap	78.97	21.03	5.19	11.99	0.13	2.82	65.10	14.77
Vigorata	none	77.02	22.98	4.14	8.99	0.38	2.99	72.70	10.80
Vigorata	burlap	79.14	20.86	4.49	10.10	0.20	2.75	70.39	12.27
White elephant	none	78.73	21.27	4.75	9.63	0.49	3.03	67.88	14.22
White elephant	burlap	80.72	19.28	5.09	14.25	0.56	3.10	64.83	12.26
Field peas:									
Gov't. No. 19788	none	6.87	93.13	3.31	28.52	1.49	5.30	53.83	7.55
Gov't. No. 19788	burlap	6.94	93.06	3.41	34.30	1.12	4.73	51.16	5.28
Emmer:									
Spring	none	9.96	90.04	2.63	19.43	3.33	2.72	66.90	4.99
Spring	9-oz. ducking	9.28	90.72	2.86	21.82	1.85	1.56	66.13	5.78
Wheat:									
Winter	none	10.19	89.81	1.94	18.94	2.79	4.39	66.92	5.02
Winter	9-oz. ducking	9.95	90.05	2.40	20.13	2.68	3.64	66.46	2.69
Spring	none	8.77	91.23	2.05	18.17	1.74	2.85	66.78	8.41
Spring	burlap	8.70	91.30	3.22	27.80	2.04	3.24	59.24	4.46
Sonora	none	8.49	91.51	1.83	18.73	2.21	2.23	68.84	6.16
Sonora	burlap	8.71	91.29	2.09	19.92	2.06	2.60	66.85	6.48
Oats:									
Sixty-day	none	6.96	93.04	5.14	18.00	4.84	9.51	49.72	12.79
Sixty-day	burlap	6.69	93.31	4.91	20.04	4.03	9.03	48.32	13.67
Barley:									
Bearded	none	8.22	91.78	3.08	19.64	2.57	4.77	62.86	7.08
Bearded	burlap	8.10	91.90	3.10	23.67	2.10	4.83	59.25	7.05
Hullless	none	8.76	91.24	2.43	18.30	2.90	2.30	67.17	6.90
Hullless	burlap	9.43	90.57	2.76	20.08	2.62	2.14	65.19	7.21

These results show the following effects of the shading:

The moisture content is increased or, conversely, the percentage of dry matter is decreased, in the shaded plants. This is not noticeable in those plants which, like the peas and cereals, become very nearly dry in maturing, but is quite apparent in the potato tubers.

The percentage of mineral matter or "ash" is higher in the shaded samples in every pair except one, the oats. Other pairs of oats than that included in the table showed an increased percentage of ash in the shaded sample, however. Hence the single exception in the table may be regarded as the only exception to the general rule which has been found in our work.

The percentage of crude protein is higher in the shaded sample in every case. The average increase is about 10 per cent. of the total found in the unshaded sample but in certain individual cases in the potatoes and the wheat it rises to nearly 50 per cent.

The fat content (ether extract) is generally lower in the shaded samples, but there are occasional exceptions. The differences in either direction are usually small and are probably without very much significance. At least, it will take further experiments, using plants which elaborate larger proportions of ether-soluble matter, to afford conclusive evidence as to the effect of shade on this constituent.

The acid- and alkali-insoluble matter, conventionally designated as "crude fiber," appears to show no regular effect of the shading, being sometimes slightly higher and sometimes slightly lower in the shaded sample.

[1] *J. Am. Chem. Soc.*, **29**, 764–767 (1907).

The percentage of starch, as determined by acid-hydrolysis, is invariably lower in the shaded sample. But, contrary to our expectations, the effect upon the starch content is less marked than that upon the mineral and nitrogenous matter. In no case is the proportional decrease in starch equal to the corresponding increase in the other two constituents.

The column headed "undetermined" represents the difference between the total of the five proximate constituents as determined by the official methods and 100 per cent. What this undetermined constituent may be or whether it is simply carbohydrate matter not accurately estimated by the admittedly empirical methods of analysis is a question which many investigators have as yet failed to solve. However, if the last three columns were totaled and reported simply as "carbohydrates," the effect of the shading upon this constituent group would be identical with that shown by the starch determinations in every case.

In brief, then, it may be said that the shading, whatever the texture of the material used or the length of the shading period, caused an increase in the percentage of moisture, mineral matter, and nitrogenous matter, and a decreased percentage of starch or carbohydrates. But the increase in other constituents is not directly proportional to the decrease in starch. Hence, we conclude that the changes produced by the shade are not simply a deterrence of the elaboration of starch or carbohydrates in the absence of direct sunlight, but other physiological changes are induced by the shading. This opens an interesting field for study by the plant physiologist. That the attention of other investigators is being attracted to this problem is shown by the recently published results of Lubimenko[1] and the controversy between Rawson and Ingle and Evans[2] as to whether observed changes in composition are actually due to differences in available sunlight or to changes in temperature induced by the shading medium.

The thanks of the writer are due to Mr. H. R. Watkins and to Mr. Geo. A. Olson for the analytical work reported in this article.

Laboratory of the
State Agricultural Experiment Station,
Pullman, Wash.

[1] *Bull. Acad. St. Petersb.* **1907**, 395–426; and *Compt. rend.*, **144** (May, 1907), 1060.

[2] *Transvaal Agr. Jour.* **4** (1906); **75**, 558–566; **16**, 743–754; and **17**, 140–148

POTASSIUM-IODIDE-STARCH PAPER.

By C. G. Storm.

Received September 20, 1909.

The facts which are noted in the literature of explosives concerning the potassium-iodide-starch paper used in the heat test or Abel test, are found to be misleading in many cases, particularly as to its keeping qualities and the effect of light on the paper. The following work on this subject was carried out by the author while in charge of the chemical laboratory of the Navy Smokeless Powder Works, at Indian Head, Md. Heat test paper prepared in this laboratory with proper precautions and preserved in tight stoppered dark bottles has been found in perfect condition after a period of eight years.

The method of preparation is about the same as that usually employed, except that the paper before treating is washed for only a short time in distilled water (dipping for about 10 seconds), also the potassium iodide and starch solutions are cooled before mixing.

The paper used is Schleicher and Schüll's 597. This quality of paper weighs about 5 grams per 100 sq. in. It is cut in strips about 24″ x 6″, and after washing hung on clean cords over night to dry in a room free from fumes.

The best quality of potassium iodide obtainable is recrystallized three times from hot absolute alcohol, then dried and 1 gram dissolved in 8 oz. distilled water. Corn-starch is well washed by decantation with distilled water, dried at a low temperature, 3 grams rubbed into a paste with a little cold water and poured into 8 oz. boiling water in a flask. After boiling gently for ten minutes, the starch solution is cooled and mixed with the potassium iodide solution in a glass trough.

The washed and dried paper is then at once dipped in this mixture, immersing each strip for about 10 seconds, and hanging one end over a clean cord to dry. The dipping is done in a very dim light and the paper left over night to dry in a perfectly dark room. Every precaution must be taken to insure freedom from contamination in preparing the materials, and absence of laboratory fumes which might cause decomposition. When dry, the paper is cut into pieces about 1″ x 3/8″ and preserved in tight glass-stoppered bottles, the edges of the large strips being first trimmed off about 1/4 in., to remove portions which are sometimes very slightly discolored. The finished paper should be of good white color. It has been found

that the test paper will invariably give a coloration with acetic acid, the intensity of the test depending on the strength of the acid used. In the report of His Majesty's Inspector of Explosives, for 1907, it is stated that washing the paper in 10 per cent. acetic acid and then in water, before dipping in the KI-starch solution, removes impurities from the paper, thus preventing the discoloration in the acetic acid test. These results have not been confirmed by experiments made by the author.

The method of testing relied on is that of comparing the new paper with regular stock paper which has been found satisfactory. This is done by making comparative tests at 65.5° C., on the same sample of nitrocellulose, under as near as possible the same conditions, a series of five tubes of the sample containing varying amounts of moisture being used for each test and the minimum test of each series noted. A new lot of paper is usually tested within one week after preparation and should give results agreeing closely with those of older lots.

In the following tables are noted the results of comparisons of different papers of widely varying age.

Date of preparation of paper.	Age of paper at time of test.	Nitrocellulose. Lot No.	Heat test at 65.5 C. Min.
12– 7–06	3 months	2462	44
6– 8–06	9 months	2462	46
5–30–06	10 months	2462	44
4–19–06	11 months	2462	44
3–19–06	1 year	2462	44
6–28–05	1 year, 9 months	2462	47
3–18–05	2 years	2462	43
2–10–02	5 years	2462	43
Jan. –03	3 months	914	36
Apr. –00	3 years	914	32
9–25–08	5 months	3505 D	34
9–10–07	1 year, 5 months	3505 D	36
6– 8–06	2 years, 8 months	3505 D	35
6–27–05	3 years, 8 months	3505 D	35
8–12–04	4 years, 6 months	3505 D	35
5–23–03[1]	5 years, 9 months	3505 D	21
10–11–02[1]	6 years, 4 months	3505 D	20
7–19–01	7 years, 7 months	3505 D	34
10–24–00	8 years, 4 months	3505 D	33
4– 2–07	2 months	Sample X	26
6–21–07	6 days	"	26
10– 5–07	10 days	2812	43
9–10–07	35 days	2812	45
11–12–07	1 day	2855	51
6–21–07	5 months	2855	50
2– 8–07	1 day	2446	50
12– 7–06	2 months	2446	50
12– 7–06	2 days	2377	56
6– 8–06	6 months	2377	52
12– 7–06	1 ½ months	2413	43
6– 8–06	7 ½ months	2413	45
12– 7–06	1 ½ months	2401 B	16
6– 8–06	7 ½ months	2401 B	18

[1] (NOTE.—The papers of 5-23-03 and 10-11-02 were preserved wrapped in paper and placed in a tin box with loosely fitting cover, within a closed drawer. The low test is undoubtedly due to deterioration.)

Except where noted, all samples had been kept in tight glass-stoppered black bottles since manufacture, being opened only occasionally for the purpose of taking out a supply of paper.

From these results it is evident that potassium-iodide-starch paper, when properly prepared, is in condition for use within 24 hours after dipping, and when properly preserved will remain in good condition practically indefinitely.

To determine the effect of light, a batch of test paper was divided up in four bottles of different colored glass plain colorless, amber, blue and black (opaque), the bottles tightly stoppered and sealed, and placed in a window ledge receiving good light but not direct sunlight. After three weeks' exposure, the same lot of nitrocellulose was tested with paper from each bottle and also from the regular stock paper. Results of test:

Paper.	Heat test at 65.5° C. Sample A. Min.
Regular stock	59
Colorless bottle	48
Amber bottle	60+
Blue bottle	60+
Black bottle	60+

The bottles were then exposed to direct sunlight for a total of 106 hours and samples of nitrocellulose tested with each paper as before:

Paper.	Heat test 65.5° C. Sample B. Min.	Sample C. Min.
Regular stock	21	45
Colorless bottle	20	46
Amber bottle	20	51
Blue bottle	20	44
Black bottle	20	50

During a further exposure to light for two months, a large portion of the time to direct sunlight, the blue and brown bottles were broken. Tests of the other samples were as follows:

Paper.	Heat test 65.5° C. Sample C. Min.
Regular stock	45
Colorless bottle	48
Black bottle	44

Apparently the action of light on heat test paper for even considerable periods is not in the least deleterious, provided there is no contact with moisture or fumes. There are reasons, however, for the belief that the paper, when freshly prepared, is more sensitive to the action of light than after it has aged for a time.

U. S. GEOLOGICAL SURVEY
TECHNOLOGIC BRANCH,
PITTSBURG, PENNA.

POTASH TESTS IN COMMERCIAL FERTILIZERS.[1]

By J. E. Breckenridge.

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The fact that potash tests in fertilizers as carried out by the methods of the Association of Official Agricultural Chemists are low seems to have been well established.

To determine where this loss occurs and what conditions effect this loss, in 1906 I made the following experiments:

Exp. No.		Theory. Per cent. K_2O.	Results by official method. Per cent.	Loss. Per cent.
1	Fresh acid phosphate and muriate of potash	6.23	6.06	0.17
2	Fresh acid phosphate and high-grade sulfate of potash	6.28	5.98	0.30
3	Fresh acid phosphate and double manure salt	7.09	6.79	0.30
4	Fresh acid phosphate and 30 per cent. salt	8.48	8.31	0.17
5	Fresh acid phosphate and 20 per cent. salt	10.19	10.00	0.19
6	Fresh acid phosphate and muriate of potash and 7 per cent. $CaCO_3$	6.23	6.07	0.16
7	Fresh acid phosphate and muriate of potash and 7 per cent. $CaCO_3$ and 6.5 per cent. sulfate of iron	6.23	5.84	0.39
8	Fresh acid phosphate and muriate of potash and 7 per cent. $CaCO_3$ and 6.5 per cent. iron and aluminum phosphate rock	6.23	5.90	0.33
9	Fresh acid phosphate and muriate of potash and 6.5 per cent. $CaCO_3$ and 6.5 per cent. sulfate of iron and 6.5 per cent. NaCl	6.23	6.11	0.12
10	Fresh acid phosphate and 30 per cent. salt and $CaCO_3$ and 6.5 per cent. sulfate of iron	8.46	7.87	0.59

The materials used in experiments Nos. 1, 2, 3, 4 and 5 were weighed into flasks, water added and the whole boiled for one hour, then proceeded as in official method.

The materials used in experiments Nos. 6, 7, 8, and 9 were weighed into flasks and water added to a paste and heated to 212° F. for 20 hours, then proceeded as in official method.

The materials used in experiment No. 10 were weighed into flask and water added to a paste and allowed to stand longer than experiments Nos. 6, 7, 8 and 9—about three days on top of a steam bath—then analyzed by official method.

Remarks.—Potash salts having no chlorine, as high-grade sulfate of potash and double manure salt, give greater loss than muriate of potash, 20 per cent. and 30 per cent. salts.

Compounds of iron and aluminum and lime have the greatest effect in giving low potash results.

Excess of chlorides lessens this loss as in experiment No. 9, due, I believe, to hydrochloric acid formed by the action of the phosphoric acid in the acid phosphate on the muriate. Any insoluble compounds which might form by the action of the soluble potash on the insoluble material in the rock, especially the silicates of iron, alumina and lime, would at once be dissolved by the hydrochloric acid formed and having ammonium chloride in the solution, when the ammonia and ammonium oxalate are added, the occlusion of potash would be somewhat prevented.

Further investigation led to the following experiments in 1908 and 1909:

Experiments with known amounts of acid phosphate and muriate of potash, allowing the solution as made by the official method, and having had the ammonia and ammonium oxalate, to stand different times before filtering:

Weighed into a 500 cc. flask 9 grams of acid phosphate, testing water-soluble potash 0.02 per cent., and 1 gram muriate of potash, testing water-soluble potash 51.70 per cent. Proceeded as in official method, allowing solution, having had the ammonia and ammonium oxalate, to stand before filtering:

	Result. Per cent. K_2O.	Theory. Per cent.	Loss. Per cent.
2 hours	4.84	5.19	0.35
24 hours	4.94	..	0.25
72 hours	5.06	..	0.13

Mr. M. H. Pingree, in a paper before this Society at Baltimore, in 1908, found that in allowing the solution to stand two weeks before filtering, the theoretical amount of potash would be found. His results were:

"Sample of acid phosphate and sulfate of potash, analyzed by official method, allowing solution having had the ammonia and ammonium oxalate to stand.

	Per cent. K_2O.	Theory. Per cent.	Loss. Per cent.
Ordinary time gave as a result	5.04	5.45	0.41
1 week	5.39	..	0.06
2 weeks	5.41	..	0.04

Sample, sulfate of potash, fish, acid phosphate and blood gave by official method:

	Per cent. K_2O.	Theory. Per cent.	Loss. Per cent.
Standing ordinary time	5.31	5.62	0.31
1 week	5.48	..	0.14
2 weeks	5.62	..	None

There seems to be a secondary reaction, by which the lost potash goes into solution on long standing in presence of ammonia.

[1] Read at meeting of American Chemical Society, Detroit, 1909.

The weight of sample was reduced to 5 grams in a 500 cc. flask and the official method was followed, allowing solution to stand two hours before filtering. Result:

4.89 per cent. K_2O on theory of 5.19 per cent. Loss, 0.30 per cent.

The following method was tried, which we shall call B, using 5 grams for weight:

Method B.—Placed sample of fertilizer on a 11 cm. filter paper and washed with small portions of cold water into a 500 cc. flask if 5 grams were amount of sample taken, and into a 200 cc. flask if 2 grams were taken, until the flask is about four-fifths full.

Added to washings in the flask 5 cc. hydrochloric acid (concentrated), heated to boiling, made alkaline with ammonia, added ammonium oxalate, cooled at once and filtered and proceeded as in official method. Result:

5.06 per cent. K_2O on a theory of 5.19 per cent., making loss of 0.13 per cent.

Remarks.—We shall notice that washing the sample on filter reduces our loss to 0.13 per cent. K_2O on a theory of 5.19 per cent., while the official method gave us a loss of 0.35 per cent.

To find whether the materials insoluble in acid, as we find them in phosphate of rock, cause this loss, or whether the precipitation by ammonia and ammonium oxalate in the absence of these insoluble materials causes the loss, or both, the following experiments were made:

Experiments with Water Solution of Acid Phosphate and Water Solution of Muriate of Potash, with and without Carbonate of Lime and Hydrate of Lime.—Solution No. 1: 20 grams acid phosphate in 300 cc. of water, heated and filtered into a 500 cc. flask and residue washed to 500 cc.

Solution No. 2: 4 grams muriate of potash in 200 cc. flask, dissolved in water and made to mark.

Exp. No.		Theory. Per cent K_2O.	Result.	Loss. Per cent.	Gain. Per cent.
1	Added 50 cc. of solution No. 1 and 10 cc. of solution No. 2 in 200 cc. flask and proceeded as in official method..............	5.19	5.11	0.08	..
2	Added 50 cc. of solution No. 1 and 10 cc. of solution No. 2 and 0.05 gram $CaCO_3$ in 200 cc. flask and proceeded as in official method	..	5.16	0.03	..
3	Added 50 cc. of solution No. 1 and 10 cc. of solution No. 2 and 0.05 gram $CaCO_3$ and 0 6 gram citric acid in 200 cc. flask and proceeded as in official method....	..	5.20	..	0.01
4	Added 50 cc. of solution No. 1 and 10 cc. of solution No. 2 and 0.05 gram $CaCO_3$ and 2 cc. hydrochloric acid in 200 cc. flask and proceeded as in official method	..	5.20	..	0.01
5	Added 50 cc. of solution No. 1 and 10 cc. of solution No. 2 in 200 cc. flask, added ammonia in excess, then hydrochloric acid to slight acidity to clear the solution, heated, added ammonium oxalate, cooled and proceeded as in official method. The filtrate showed no further precipitate with ammonia, showing a good separation of lime	..	5.09	0.10	..
6	Added 50 cc. of solution No. 1 in 200 cc. flask, added dry $CaCO_3$ to neutralize, if possible, the acidity. The acidity was not destroyed by excess so $Ca(OH)_2$ was added until solution was alkaline, then 10 cc. of solution No. 2 were added, and proceeded as in official method...........	..	5.04	0.15	..

This was to see if calcium phosphate precipitated would occlude any potash when the insoluble material of the acid phosphate was absent.

Remarks.—There seems to be some loss when the insoluble material of the acid phosphate is absent. Addition of hydrochloric acid or citric acid, as in experiments Nos. 3 and 4, seems to overcome this loss.

Experiments to Show the Effect of Magnesium Salts, Iron and Lime Salts when Present in Solutions of Acid Phosphate and Potash, the Insoluble Material of the Acid Phosphate being Absent.—Solution No. 1: Water solution of acid phosphate 40 grams to 500 cc. of water.

Solution No. 2: Water solution of muriate of potash 8 grams to 200 cc

Exp. No.		Theory.	Result.	Loss Per cent. K_2O.
1	Added 50 cc. of solution No. 1 and 0.5 gram $Ca(OH)_2$ and 10 cc. of solution No. 2 and 0.25 gram $MgSO_4$ in 200 cc. flask and proceeded as in official method............	5.19	5.12	0.07
2	Same as No. 1 only used $MgCl_2$ instead of $MgSO_4$..................................	..	5.07	0.12
3	Same as No. 1 and No. 2 only used sulfate of iron instead of magnesium salts......	..	5.01	0.18

Remarks.—Iron seems to have a little effect on losing potash in these tests, magnesium salts not so much as iron.

Inasmuch as the insoluble in acid in phosphate rock becomes the insoluble in water, to a large extent, in acid phosphate, the following experiments, with different grades of phosphate rock and muriate of potash solution, were made to find the effect on losing potash when the official method is used:

These experiments were made by adding the materials together in a 200 cc. flask and proceeding as by official method for potash.

Results should show evaporating 25 cc. of solution 6.37 per cent. K_2O.

Experiment No. 1.

		Per cent.
1 gram muriate of potash		
5 grams of phosphate rock, testing	Insoluble and sand	9.30
	Iron and alumina	2.45
	Bone phosphate of lime, dry basis	68.18

Potash determined at once as soon as solution was cold after adding ammonia and ammonium oxalate.

	Result.	Loss. Per cent. K_2O.
About 2 hours' standing	6.23	0.14
After 24 hours' standing before filtering	6.15	0.22

Experiment No. 2.

		Per cent.
1 gram muriate of potash.		
5 grams of phosphate rock, testing	Insoluble and sand	11.20
	Iron and alumina	2.40
	Bone phosphate of lime, dry basis	65.94

		Loss. Per cent.
Potash determined at once	6.15	0.22
After 48 hours' standing	6.10	0.27

Experiment No. 3.

		Per cent.
1 gram of muriate of potash.		
5 grams of Tennessee phosphate rock, testing	Insoluble and sand	5.63
	Iron and alumina	6.20
	Bone phosphate of lime, dry basis	74.19

		Loss. Per cent.
Potash determined at once	6.10	0.27
After 48 hours' standing	6.03	0.34

Experiment No. 4.

		Per cent.
1 gram of muriate of potash.		
5 grams of rock, testing	Insoluble and sand	5
	Iron	12
	Alumina	21
	Phosphoric acid	45

	Per cent.	Loss. Per cent.
Potash determined at once	5.91	0.46
After 48 hours' standing	5.92	0.45

CONCLUSIONS.

That as the insoluble in acid in phosphate rock increases, the loss in potash increases.

Phosphate rock having moderate amount of insoluble material and high iron and alumina as in experiment No. 3 has decided effect in losing potash.

Large amounts of iron and alumina with even moderate amounts of insoluble, as in experiment No. 4, where we have about 12 per cent. iron, 21 per cent. alumina, 5 per cent. insoluble material, have the most effect on losing potash.

Is it not reasonable to believe that what has caused this loss is similar to that which takes place in potash solutions in contact with soils, when the potash becomes fixed by the iron, alumina and silica?

Such being the conditions there seems to be great chance for rendering water-soluble potash insoluble when we add water to our samples and boil as in official method.

Washing away as soon as possible the soluble material from the insoluble material of fertilizers seems but a reasonable way of overcoming somewhat this possibility of losing potash in our methods.

Comparing official method with method B as given before, we have:

Sample No. 1.—Acid phosphate having about 5 per cent. iron and aluminum oxides.

Sample No. 2.—Muriate of potash testing 51.70 per cent. K_2O.

Exp. No		Result. Per cent. K_2O.	Loss. Per cent.
1	Weighed into 500 cc. flask 9 grams sample No. 1 and 1 gram sample No. 2 and analyzed by official method	4.70	0.47
2	Weighed 4.5 grams of sample No. 1 and 0.5 gram sample No. 2 on to filter paper and analyzed by method B	5.03	0.14

Sample of 7 per cent. potash goods, representing about 600 tons, gave by official method 6.70 and 6.72 per cent. K_2O, by method B, 7.10 per cent. K_2O.

For samples having large amounts of organic matter hot water should be used for washing in method B in place of cold water.

Laboratory of American Agricultural
Chemical Company,
Carteret, New Jersey.

ADDRESSES.

THE DYNAMIC VIEWPOINT OF SOILS.[1]

By Frank K. Cameron.

Within the past decade or decade and a half there has been a marked revival of interest in soils and soil fertility. This has led to the advancement of a number of theories, most of which have the attractive characteristics of apparent simplicity, *i. e.*, they attribute fertility or lack of fertility to some one or perhaps two causes. Another remarkable feature of most of these theories is the certainty and sureness of tone with which they are announced. For instance, one of the most prominent of American agronomists stated in a recent letter that "The currently accepted theory is that the principal factor in the loss of fertility is the loss of humus and nitrogen, and the data at hand seems to me to leave this theory as yet quite competent to explain the facts." And within the past few months we have been advised that "Phosphorus is already the element that limits crop yields on those great soil areas in the corn belt,

[1] Published by permission of the Secretary of Agriculture. Abstract of an address prepared for the Division of Food and Agricultural Chemistry at the Detroit meeting.

in the wheat belt, and in the cotton belt, which are producing and must produce the great bulk of the crops required to feed and clothe the American people."[1] And we are told further: "The supply of nitrogen in the air is absolutely inexhaustible; and the supply of potassium in all normal soils is also practically inexhaustible (potassium can also be recovered if necessary from the ocean's inexhaustible supply); and our deposits of limestone are surely inexhaustible; whereas our total supplies of phosphorus are extremely limited, not only in our most important soils, but also in our natural phosphate deposits, and phosphorus is not contained in the air or in the sea." One cannot help wondering where the fishes get the material for their bones; and if the phosphorus does not go to the sea, where it does go; and why, with good and valid reasons at hand for urging the conservation of our phosphate deposits, this particular argument should have been advanced.

In spite of the agronomist cited above, probably the most widely accepted theory of soil fertility is that known as Liebig's "law of the minimum," which may be stated as follows: Of the mineral elements needed by a plant, that one which is present in the soil in the smallest ratio to the amount needed by the plant, determines the productivity of the soil with regard to that plant. It is further assumed popularly that this law has practical application only with respect to the soil content of phosphoric acid, potash and nitrogen, although Hall[2] would apparently apply it to the moisture content and physical characteristics of the soil also.

To justify this law it is postulated (1) that soils are usually so deficient in phosphoric acid, or potash or nitrogen that the growing crop cannot obtain enough to maintain efficiently its metabolic processes, and, (2) to get around the analytical results from soils and plants; it is further postulated that the mineral plant food elements exist in the soil in two types of compounds or minerals, available, *i. e.*, soluble and non-available or insoluble.

All these theories, however, are formulated from a static viewpoint of the soil. Their supporters look upon a given field of soil as a fixed, stationary mass of material which remains in place indefinitely, except in so far as some of the constituents are carried away in drainage waters or removed by garnered crops. Therefore, it is argued, since crop roots feed in a limited volume of soil, say the first seven inches, and any given analysis shows so many pounds of phosphorus in the acre seven inches deep, while the crop takes out so many pounds per year, the soil cannot last (*i. e.*, produce crops) longer than so many years, determined by simple division. In order to maintain crop yields it is only necessary to keep adding the amounts of mineral matter as they are removed.

In the present stage of our knowledge, the problem is not, unfortunately, so simple. In studying the relation of plant growth to soils we must consider three things: *viz.*, the plant, or at least the plant roots; the soil moisture, the great natural nutrient medium from which plants draw their mineral sustenance; and the solid particles of the soil.[3] Under field conditions all three of these are constantly moving. If the plant roots cease to move, the plant dies. It is inconceivable that the soil moisture should cease to move; when it rains some of the water runs over the surface and into the regional drainage, some evaporates into the air, and some goes into and through the soil. As McGee aptly puts it, these are the "run-off," the "fly-off" and the "cut-off." The "cut-off" passes through the soil, by way of the larger openings, mainly by gravitation; some of it passes out through seepage, etc., to the regional drainage, but some of it remains to rise again towards the surface through the capillary openings of the soil and in films over the surfaces of the soil grains, to ultimately join the fly-off.

[1] *University of Illinois, Agr. Exp. Sta., Circular* **127** (1909).

[2] *Science*, **28**, 617 (1908).

[3] The soil atmosphere, bacteria, and lower life processes are all dynamic problems obviously, but are not included here specifically, since their several effects are integrated in the factors cited.

There is also much evidence that the solid particles themselves are in constant motion as a result of the action of forces internal to the soil mass. For instance, it has been shown that the structure of the soil and the mutual arrangement of its component particles is dependent upon the character of the moisture films surrounding and connecting these particles, and therefore upon the amount of water which is present.[1] The constant change of water content of the normal soil must therefore produce equally frequent changes in the soil structure, with accompanying movements of the particles among themselves. These movements become obvious through the well-known and considerable changes in the volume of soils on wetting or drying, succeeding changes in opposite directions being marked by a noticeable hysteresis or by never being exactly equivalent. The distances through which the soil particles are moved by a single change of water conditions are probably very small, but it is evident that there is here an efficient agency for the continual mixing of the soil itself, and that in time there must be some interchange of material between adjoining masses of soil and between the soil and the subsoil. It is claimed by some authorities that this process tends to segregate the finer particles of the soil at lower depths, but as to this I am not personally certain. It is certain, however, from controlled experiments and observations that the soil motions due to change in the amount and distribution of liquid water are much more important than is popularly supposed, and the still greater motions due to freezing and thawing are matters of common knowledge. The "cracking" of a soil on drying out is another matter of common observation. These cracks are usually of considerable depth, extending to or into the subsoil. The breaking away of the surface soil at the edges of these cracks is by no means an inconsiderable factor in mixing soil and subsoil, tending to bring gradually the latter material nearer the surface.

In every soil in which a crop can grow at all there is a constant bringing of material from the subsoil to the surface of the upper layers of the soil through the activities of earth worms, burrowing mammals, ants, etc. This continual interchange of material between soil and subsoil is undoubtedly very large in the aggregate. Tillage methods, especially plowing, are for the express purpose of breaking up and loosening the soil, and when properly conducted, greatly facilitate the spread of plant roots through the soil, and add to the movements of the soil particles themselves.[2]

[1] *Bulls.* **10** *and* **50**, *Bureau of Soils, U. S. Dept. Agr.*

[2] The inherent power of a root to push itself through a soil, or "root penetration" as it is often styled, if existent at all must generally be exceedingly small, otherwise destruction of the plant tissue would result inevitably. Root penetration must be due to the continued movement of the soil particles, the expanding root merely taking advantage of these movements due in most cases probably to the continually changing thickness of the water films on the soil grains.

The flow of water across the soil surface always produces some motion of the soil particles from place to place—small in some instances, very large in others. In our rolling lands, where stone fences are usual, frequently the soil is higher on the uphill side of the fences than on the lower; or, on more level lands, on the side from which the prevailing wind blows; and this is true even in lands which are under sod or other protecting vegetable covering for a large part of the time. No less important probably than any other agency is the wind, which is blowing to some extent all the time and which carries into the air soil material to be deposited elsewhere, even at great distances. The carrying power of the wind is now known to be very great. For instance, soil material from the Sahara desert is frequently observed to deposit in Europe, even to considerable latitudes. Certain of our loessial deposits are striking examples, but it is no less certain that on every field, and especially on cultivated fields, there is an annual removal from the surface of considerable amounts of soil material which is deposited elsewhere, and contrariwise, every field is constantly receiving more or less soil material from other areas, frequently at a great distance. Professor Udden,[1] in what appears to be a conservative calculation, finds that the carrying power of the winds of the Mississippi Valley into the Gulf of Mexico is about 1,000 times that of the Mississippi River (about 340,500,000 tons annually),[2] and the carrying power of the winds over most of the area of the United States, for instance, is of the same order of magnitude. I would not be understood to assert that the actual translocation of soil material by wind is so great as this, but it is undoubtedly very large indeed, and a most important factor affecting the mineral composition of the soil in determining its markedly heterogeneous character with regard to the distribution of rock-forming minerals. The wind is probably the principal agent in making soils far richer in the variety of minerals present than are the rocks from which they are derived.

Space will not permit me to develop further our knowledge of these motions of the soil, and it is not necessary, for they are well known to scientific men generally, and presumably are the common property of all soil investigators. What I have cited is sufficient to remind one that there are forces continually at work changing the actual mineral composition of the surface soil, and that these changes are not only continuous but of an important magnitude. The claim of support from the geologists, sometimes made by the upholders of the static theories, on the ground that the age of the soil is measured by the rate at which some one or more of the elements increase in percentage with depth of soil, is ill founded, and it is very doubtful if any present-day geologist of repute would make or countenance such an argument, any more than any one who has kept pace with modern development in soil work would claim that the potash and phosphoric acid content of the soil would necessarily measure its producing power. An increase of 50 per cent. of fine quartz sand to the soil, for instance, would not necessarily lower its crop-producing power, but might even increase it considerably, although it would lower the percentage of phosphorus and potassium present in the sample.

Returning to the consideration of the soil moisture, it seems obvious, and has been experimentally verified in the laboratory a number of times, that the water passing down through a soil under gravitational force dissolves and removes but a small portion of the mineral content. Since this water does not remain long in contact with the soil grains the diffusion of dissolved material from the solution in the finer spaces and the soil films is slight. Our springs, creeks and rivers generally have a low and widely varying mineral content, lower in fact than the mineral content of the extract made by shaking up the surface soil with a small portion of water. On the other hand, with the advent of fair weather conditions, and the consequent evaporation at the surface, the "cut-off" water in returning to the surface through the capillary spaces and the films on the surfaces of the soil grains, is longer in contact with the minerals, and dissolver much more of them and thus it carries towards the surface a relatively large amount of the mineral constituents of the soils. Under ordinary conditions in humid climates, the concentration of the soil moisture is very largely controlled by absorptive phenomena, which are now pretty well understood, which have been the subject of exhaustive investigations, and which are readily accessible to all soil investigators.[1]

In opposition to this view there has been cited the removal of lime from certain fields at Rothamstead.[2] But this data is no more pertinent to a normal case than would be the accumulation of alkali under arid and semi-arid conditions. The Rothamstead soils are unusual in containing a very large percentage of lime carbonate; at least this is true of the Broadbalk soils, which I have personally examined. Under the very humid conditions obtaining in England, and under good drainage, it is natural to expect that the surface accumulations of lime would be lowered just as much as would be the case with the sodium chloride content if large masses of rock salt were harrowed into these soils. What one would expect in due course of time would be an adjustment between the amounts of lime carried out by the drainage waters and the amounts rising from the lower depths by the capillary rise of the soil water. The results obtained at Rothamstead are in no wise out of harmony with, but are in accord with and tend to confirm the views above expressed.

The static viewpoint leads its supporters to consider that the one function of a fertilizer is to add needed plant food to the soil, although usually they admit that some minor physical effects may be produced. The dynamic viewpoint leads to the conclusion that fertilizers have probably many other functions; that, in fact, the cases where they are useful *merely* as sources of plant food are probably exceptional. What all the functions of fertilizers are, I do not pretend to know, although I have given to the problem nearly ten years' earnest study with unusual facilities at my command. Fertilizers certainly do affect the physical properties of soils, although in the majority of cases these effects may be of minor importance in influencing plant growth.[3] It is

[1] *Jour Geol*., **2**, 318 (1894).

[2] "Deandation," by R. B. Dole and H. Stabler, *Water Supply Paper*, **234**, U. S. Geological Survey, Dept. Interior, 1909.

[1] *Bulls*. **30**, **51** *and* **52**, *Bureau of Soils, U. S. Dept. of Agr.*

[2] *Science*, **28**, 866 (1908).

[3] That the physical effects produced by fertilizer have not yet received adequate attention from soil investigators can hardly be gainsaid. With such amounts of mineral salts as are commonly employed, it is not easy to see how the strictly chemical processes in the soil can be seriously changed or modified. But with our increasing knowledge of the profound physical changes produced by small amounts of solutes, and especially electrolytes, as for instance in the phenomena of flocculation, sedimentation, surface tension viscosity, density of solvent.

very probable that fertilizers have a very important rôle in affecting the enzymes, and the lower plant life in the soil, fungi, molds, bacteria, etc. Convincing evidence has recently been obtained that growing and especially young plants excrete through their roots organic substances giving rise to conditions harmful or injurious to these same plants and to others of the same or closely allied species; and it has been shown experimentally that certain portions or zones of the roots show a very high oxidizing power towards organic substances, which oxidizing power is modified by the presence of various substances, being generally increased by the salts common to commercial fertilizers.[1] It has also been shown that oxidation of the organic root excreta harmful to plants generally produces substances harmless or even beneficial thereto, and it seems to me probable that *a* function, perhaps sometimes even the main function of fertilizers is to modify the oxidation of organic matter, root excreta included, in the soil. Other effects of fertilizers than those noted have also been observed, but further mention of them would be premature. To sum up, I believe that fertilizers have physical, chemical, and biological rôles, which the "plant food" theory of fertilizers is entirely inadequate to explain. It is certainly a weak point in this theory that although it prevailed for seven or eight decades, to the practical exclusion almost of all others, it has led to no rational quantitative practice, which should be easily determinable if its premises were correct.

The use of the expression "available plant food" by the advocates of the static viewpoint appears to me to be misleading and unfortunate. This expression has an historical and academic significance in connection with the numerous efforts to develop an empirical method of analyzing the soil by extracting it with some solution or other. But as implying that the mineral nutrients do actually exist in the soil in two distinct classes, the idea is without experimental or other scientific justification. So far as we now know, the one and only method by which the plant can obtain mineral nutrients is by absorption from the aqueous solution in the soil, and is a purely gratuitous assumption that any minerals containing phosphoric acid, potassium, or lime, would not yield these constituents to water, given time enough and barring previous saturation of the solution or mechanical removal of the mineral.

Likewise, the distinction between "fertilizers" and "stimulants," which certain authors have sought to make lately, appears to me to be a begging of the question, and an unscientific attempt to "save the face" of the plant food theory of fertilizers. It must be shown that the increased plant growth obtained by adding to the nutrient medium potassium chloride or sodium chloride, respectively, involve essentially different physiological functions in the plant before this distinction will merit any serious consideration.

Again, it is a characteristic feature of the arguments usually advanced by the adherents of the static viewpoint that they are attractively simple. For instance, there has recently been advanced some mathematical deductions on the formation in the soil of monocalcium phosphate from tricalcium phosphate by the action of nitric acid there formed.[2]

etc., the conviction gains force that the physical properties of soils will need much more serious study before a rational system of fertilizer practice can be developed.

[1] *Bull.* **56**, *Bureau of Soils, U. S. Dept. Agr.*

[2] *Science*, **28**, 861 (1908).

It happens, however, that published experimental investigations, notably those of Bassett, in England, and of my own laboratory,[1] show conclusively that no such reaction could possibly take place. And even granting the argument, we are confronted at once with the need of a more rational explanation of the desirability of adding lime.

One of the more important subjects upon which the advocates of the static and the dynamic viewpoints of soils seem to take issue is crop rotation. There are very few, probably, who doubt the desirability of employing rotations, at least in general farming, and every one admits the efficacy of rotations is probably due to a number of causes, elimination of characteristic parasites, insects or plants, improvement in physical conditions of the soil by change of tillage methods incident to crops of different characters, incorporation of organic matter into the soil, etc. A majority, I think, now admit that injurious plant excreta is a probable reason for rotations. But the adherents of the static viewpoint generally hold that the main reason for crop rotation is the "exhaustion" of some one or more mineral plant food constituent in the soil, which is less necessary to the growth of the succeeding crop. On the other hand, from the dynamic viewpoint, no such hypothesis is necessary, and it is moreover highly improbable, although one may admit its possibility as an extreme and exceptional case. From the dynamic viewpoint, it is of course possible, theoretically, to imagine a rotation, which with tillage methods alone will maintain good (not necessarily the maximum) crop yields indefinitely. But no one, so far as I am aware, is advising or is ever likely to advise any such general practice. Cases might be cited where this has been followed with actually increasing yields, but they extend over too short periods of time, or are attended by other special conditions, which would make it rash to draw any general conclusions from them as yet. But, certainly, a recent extreme statement, from the static viewpoint, *viz.*, * * * * "but the effect of crop rotation is always to reduce and never to augment the total supply of mineral plant food in the soil and subsoil," is going entirely too far; is in fact, a conclusion from *à priori* premises of more than doubtful validity, and is not susceptible of experimental verification. A comparison of many thousands of analyses of European and American soils shows that on the whole the much longer cropped European soils are somewhat richer—certainly as rich—in the so-called mineral plant foods as are the American soils.[2] I am not able to see, whatever the prevailing mode of cropping may be, that there is any general or consistent evidence that soils are becoming exhausted of their mineral plant nutrients. The causes of "exhaustion" lie deeper and their explanation must be sought elsewhere.

Another popular impression sometimes assumed as a further proof of the arguments from the static viewpoint is that crop yields are going down. So far as I know, however, every one who has *investigated* the subject has inclined to the opposite conclusion. As every one knows, the popular impression has been strongly urged recently, and I am advised that the Conservation Commission sent out queries as to the yield of crops and land values to about 30,000 representative farmers, approximately 10 to each county in the

[1] For references and detailed discussion, see *Bull.* **41**, *Bureau of Soils, U. S. Dept. Agr.*

[2] *Bull.* **57**, *Bureau of Soils, U. S. Dept. Agr.*

United States, and the replies were overwhelmingly to the effect that both crop yields and land values were increasing throughout the country. Our own government statistics for the past forty years show the average crop yields are increasing in areas where fertilizers are not used as well as in areas where their use is common. European statistics, which extend back from one to several centuries, not only establish that crop yields are increasing there, but that the great improvements came before the general introduction of commercial fertilizers. The reasons for these facts I will not take space to discuss here, since the whole question will soon be presented in detail elsewhere.

At present, soil chemistry is not simple. Leaving aside such special cases as wind breaks, glass houses, etc., we have three general methods of soil control: *viz*., cultural methods, about which we have a fairly satisfactory knowledge; crop rotation, about which our knowledge is extensive and steadily increasing—although it must be confessed, it is largely empirical; and thirdly, the use of soil amendments or fertilizers, about which our knowledge is yet meagre, but increasing slowly. It is, of course, patent to every one that fertilizers sometimes, in fact frequently, produce larger crop yields. Sometimes the contrary is true, but it is absolutely certain that at the present time no one can, nor are there any methods available by which one can, safely predict what fertilizers and how much should be used. In the past, three methods of examination have been in vogue: the analyses of soils, the analyses of plants, and plot and field experiments. All of these have had their uses, all have their limitations. Space forbids my discussing them at length here, but I cite them to show that the method of attacking the problem of soil chemistry has in the past been from the analytical point of view alone. This point of view has utterly failed to give us a rational system of fertilizing. Within the last few years it has seemed desirable to some of us to attack the problem from a different point of view, bringing together the known facts about soils and fertilizers, investigating them with all the resources and pertinent methods of modern physics, chemistry and physiology. In this way alone is there hope of progress. While it is undoubtedly true that some, in fact most, of the fertilizers in common use do contain mineral constituents which are essential to plant growth, and their addition to the soil does therefore add mineral plant food, there is a large and steadily increasing mass of evidence that this can be but one function of fertilizers, and I am quite prepared to reiterate that in my judgment it is normally a very minor one.

To sum up:

1. Hitherto, the soil has generally been regarded from a static viewpoint. It now appears more rational to view it dynamically.

2. From the static viewpoint, fertilizers are valuable chiefly as sources of plant food. From the dynamic viewpoint this function is generally a minor one, and fertilizers have certainly other important functions of a physical, chemical and biological character.

3. Some advocates of the static viewpoint would make a distinction between *fertilizers* and *stimulants*. But this requires to be shown, and as now used these terms are merely a begging of the question at issue.

4. Every one believes in crop rotations. Advocates of the static viewpoint hold that it always hastens the depletion of mineral plant nutrients in the soil. This is at least doubtful.

5. The advocates of the static viewpoint hold that under copping, mineral plant nutrients necessarily disappear and soil "exhaustion" is due to this fact. But the evidence now available does not warrant these premises, and the cause or causes of exhaustion must be sought elsewhere, among others, in the character of the organic substances in the soil, and the biological processes there taking place.

6. The advocates of the static viewpoint hold that crop yields are decreasing, owing to depletion of available plant food. But crop yields are increasing and factors other than the plant food supply are the dominating ones.

7. To the advocates of the static viewpoint, soil chemistry is simple, and merely a matter of supplying enough mineral nutrients in "available" form for the crop needs. As a matter of fact, soil chemistry is a very complex subject, into which we are just beginning to get glimpses, and the supply of mineral nutrients is only one of the important details in a very intricate problem. Soil fertility will only become simple, if ever, when we have a much fuller and more comprehensive knowledge of the physical, chemical and biological processes taking place in the soil. To attain this knowledge, the soil must be regarded from the dynamic viewpoint.

BUREAU OF SOILS,
U. S. DEPT. OF AGRICULTURE,
WASHINGTON.

NOTES AND CORRESPONDENCE.

EXPERIMENTS TO FIND, IF POSSIBLE, THE POTASH IN FERTILIZERS HAVING THE POTASH FROM CARBONATE OF POTASH.[1]

In view of the fact that in analyzing by official method fertilizers having as high as 8 per cent. of potash from carbonate of potash, we do not get results equal to amount of potash added to the goods, the following work has been done:

Materials and weights used were about the same proportions as used in brands having 6 per cent. ammonia, 4 per cent. phosphoric acid and 8 per cent. potash.

Weighed the amounts independently into 200 cc. flasks.

0.25 gram carbonate potash testing...	66.56% potash soluble in water
1.30 gram cottonseed meal testing....	1.58% potash soluble in water
0.20 gram castor pomace testing......	1.08% potash soluble in water
0.25 gram bone......................	...
2.00 grams water-soluble potash by theory................ ...	9.45%

Experiment No. 1. Method D.

Same weights into 200 cc. flask, added 175 cc. cold water, a few drops of methyl orange and standard acid, hydrochloric acid, as used for nitrogen, until effervescence ceased and solution was faintly acid, then at once about 5 cc. strong ammonia, heated and proceeded as in official method. Filtered as soon as cold, which was not over two hours.

Result............ 9.14 per cent. Loss 0.31 per cent.

Experiment No. 2.

Doubled the above weights making 4 grams in 200 cc.

[1] Read at meeting of American Chemical Society, Detroit, 1909.

flask, this being the same proportions as in official method, 10 grams to 500 cc. and made these tests by official method.

Allowed solution having the ammonia and ammonium oxalate to stand

	Per cent.	Loss. per cent.
2 hours before filtering—result.	8.24	1.21
24 hours' standing—result, ...	8.88	0.57
48 hours' standing—result	9.02	0.41

Experiment No. 3.

Method E, regular official method, except we used the proportion of 5 grams to 500 cc. instead of 10 grams.

Allowed the solution, after having the ammonia and ammonium oxalate to stand 2 hours before filtering, evaporated 50 cc.

Result. . . . . 8.88 per cent. Loss, 0.57 per cent.

Experiment No. 4.

Same as No. 3 only allowed solution to stand 24 hours.

Result. . . . . 9.16 per cent. Loss, 0.29 per cent.

Experiment No. 5.

Same as No. 3 and No. 4 only allowed solution to stand 48 hours.

Result, no gain over experiment No. 4.

Tried washing 2 grams on a filter with hot and cold water and neither were satisfactory, great difficulty being experienced in washing on account of the carbonate present and results were low.

We tried burning and taking up with water and had a loss of 0.91 per cent. on 9.31 per cent. theory.

We tried burning and taking up with hydrochloric acid and still had a loss of 0.35 per cent. on 9.31 per cent. theory.

We moistened with sulphuric acid and burned and took up with hydrochloric acid and had a loss of 0.47 per cent. on 9.31 per cent. theory.

SUMMARY AND CONCLUSIONS.

Official method, 10 grams to 500 cc. solution, gives us when solution is allowed to stand before filtering:

	Per cent.	Theory, per cent.	Loss, per cent.
2 hours	8.24	9.45	1.21
5 hours	8.70	..	0.75
24 hours	8.88	..	0.57
48 hours	9.02	..	0.43

Method E, official method, only used 5 grams to 500 cc. solution proportion. When allowed to stand before filtering.

	Per cent.	Theory, per cent.	Loss, per cent.
2 hours	8.88	9.45	0.57
24 hours	9.16	..	0.29
48 hours, no gain over 24 hours.			

Method D, neutralizing 2 grams in 200 cc. flask, having 175 cc. water, with hydrochloric acid, using methyl orange as indicator, adding 5 cc. ammonia and proceeding as in official method.

After 2 hours' standing before filtering, 9.18; loss, 0.27 per cent.

Time is a great factor in factory work and we would seem to be justified in using Method D, although Method E, which is the same as official method using proportion of 5 grams to 500 cc. instead of 10 grams, gives us practically the same results by allowing solution to stand 24 hours.

J. E. BRECKENRIDGE.

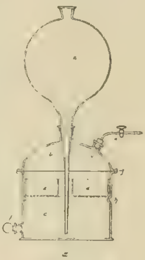
LABORATORY OF AMERICAN AGRICULTURAL CHEMICAL COMPANY,
CARTERET, NEW JERSEY.

NOTE ON A NEW MODIFICATION OF THE KIPP GAS GENERATOR.

The Kipp gas generator is undoubtedly one of the most widely used, and justly popular pieces of chemical apparatus on the market to-day, but the large number of variations of it which have been devised point to the fact that so far no thoroughly satisfactory type has been produced. My own experience with the Kipp apparatus, in the usual form sold by dealers in chemical glassware, has been that while it is admirably adapted to its specific purpose of generating various gases by the wet method, it presents certain difficulties and inconveniences in the matter of charging and cleaning. The opening allowed for the delivery tube is frequently so constricted as to render the process of charging tedious and difficult. While no very perfect cleaning is usually necessary, except in the event of the caking of the active material, washing out is always attended with some difficulty.

With the view of obviating these difficulties without interfering with the otherwise excellent properties of this apparatus, the design described on the following pages has been devised, and found successful.

In this apparatus, *a* is the usual long-stemmed acid reservoir as used in the common form of Kipp generator, and fits into the base portion with a ground joint at *i*. The base is made in two portions, the upper one, *b*, being dome-shaped, and provided with the usual tubulature, rubber stopper and delivery tube at *e*. The lower portion, *c*, of the base is cylindrical, and provided with a tubulature and glass stopper at *f*. At about two-thirds of the height of *c* from the bottom the glass is indented completely around to provide a projecting ring of glass on the inside, forming the support for the container for the active material, *d*. This container is made of porcelain or lead, and is provided with a perforated bottom, and vertical side walls. It is annular in form, having a hole in the center through which the stem of the acid reservoir passes, the wall around this hole being of the same height as that of the side walls. The two portions of the base, *b* and *c*, fit together at *g* with a ground joint, the edges of the two portions being continued outward to a flange to provide a grip for small clamps, if these are found necessary.



Modified Kipp gas generator.

The first apparatus of this type actually set up was composed of a discarded Novy jar, the acid reservoir from a broken Kipp, and a Buchner's funnel, and practically the same apparatus may be set up by any one by using a desiccator having a tubulature in the cover and a large separatory funnel. The active material may be placed upon a perforated lead plate supported on broken glass tubing or a

stand of lead or glass. With a good supply of vaseline at the ground joint g and light clamping there is practically no danger of leakage. Some additional care may be necessary in disconnecting to avoid breaking the stem of the acid reservoir; however, this is scarcely more than is necessary with the ordinary form.

The advantages claimed for this type of apparatus are:

1. Accessibility of all parts for cleaning and recharging.
2. Stability, as it is not so tall as the usual forms.
3. An even distribution of the active material over a relatively large area.

Another point in the use of gas generators of this type has come to my attention, and as it may not be known to some, I will give it here for the benefit of those who may have had difficulty along this line. It is frequently necessary to force the gas from the generator against a considerable pressure, and under these conditions it sometimes happens that the "head" of acid in the reservoir is not sufficient to entirely overcome this pressure, and the flow of gas is consequently inconveniently slow. To obviate this, I have found a good method is to connect a T-tube with the vertical arm pointing upward, between the gas chamber of the Kipp and the stopcock, and then connecting this vertical arm of the T-tube by means of a piece of stout rubber tubing, with a glass tube, the other end of which is bent so as to pass through a tightly fitting rubber stopper in the tubulature of the acid reservoir of the Kipp. Another means of attaining the same end, is to use a two-hole stopper in the tubulature on the gas chamber, through one opening of which passes the delivery tube and through the other the tube connecting with the top of the acid reservoir. In either case the gas pressure on both sides of the column of acid is kept the same, and the acid flows by gravity down upon the active material.

This principle may also be applied to the generation of gases by the dropping method, where a liquid from a separatory funnel is allowed to drop upon a solid in the bottom of a flask. It not infrequently happens that the back pressure will force the liquid back into the funnel. If the gas-filled space in the flask be connected with the upper opening of the funnel by a piece of glass or rubber tubing, the pressure on both sides will be equal, and the dropping can be regulated by the stopcock on the stem of the funnel. In using either the Kipp generator or the dropping method with this modification, a stop- or pinchcock should be provided as a relief valve at the top of the acid chamber, to be opened when the flow of gas from the generator is stopped.

A somewhat similar device has been used by Manchot and Herzog[1] and by Loevenhart and Kastle.[2]

When it is necessary to continue the generation of gas in a Kipp apparatus for some time, as in long-continued reduction, drying in hydrogen or carbon dioxide, etc., the acid is apt to become exhausted before the active material, and the addition of fresh acid to the exhausted acid is not always desirable nor feasible. By replacing the ground glass stopper at the tubulature in the base of the generator by a 1-hole rubber stopper bearing a stop- or pinchcock, and inserting a separatory funnel with a bent stem in the tubulature with the delivery tube, and then making the *a* connection between the gas chamber and the separatory through the neck of the latter, so as to equalize the pressure on both sides of the acid column, as just described, fresh strong acid may be introduced at the same time that the exhausted acid is drawn off, thus continuing the length of action without recharging. It is necessary, or at least preferable to introduce the acid this way, rather than through the acid reservoir, as the strong acid introduced through the latter channel would come directly into the current of the outgoing exhausted acid, and a large portion of it wasted.

F. Alex. McDermott.

Washington, D. C., September, 1909.

[1] Liebig's Annalen, **316**, 321 (1901)

[2] *Amer. Chem. Journal*, **29**, 427-428 (1903)

A RAPID METHOD FOR DETERMINATION OF SPECIFIC GRAVITY OF COAL.

During the routine work of this laboratory, it is necessary to determine specific gravity on a large number of samples of anthracite coal. As the methods available gave but little satisfaction commensurate with the time and labor entailed, we had recourse, after considerable experimentation, to the herein described procedure.

The apparatus, first of all, is simple, and may be found in almost any laboratory. The first requirement is a stout flask of about 250 cc. capacity, with a long and rather slender neck, terminating in a flaring mouth, such as the "copper determination" flask supplied by the Denver Fire Clay Co. This flask is to be marked at the base of the neck, either by a file scratch or by etching, and its volume up to this mark determined by means of a 100 cc. automatic pipette and a 100 cc. burette, graduated in 0.2 cc.

The burette should have a three-way stopcock, and be connected with a reservoir either below or above the level of its top. In the former case suction is used to fill the burette, while in the latter case gravity is the means. It is better to use the elevated reservoir and gravity feed for the pipette. Of course it is understood that a plain burette and pipette can be used, the form described merely having the advantage of rapidity.

The flask is calibrated as follows: The flask is rinsed with water, inverted, and allowed to drain for one minute; 100 cc. water are then added from the pipette, the flask is then filled to the mark from the burette. In calibrating by this method, inaccuracies in either pipette or burette do not militate against the accuracy of the specific gravity result, as the same method is pursued in the final determination.

The actual determination is carried out as follows: 100 grams of coal, previously crushed to about 4 mesh, and carefully sampled, are weighed to 0.1 gram, and placed in the flask. 100 cc. water are run in, a 1-hole stopper fitted with bent glass tube and rubber connection is inserted in the mouth of the flask; suction is applied, and the flask is shaken, care being taken that no water is splashed into the glass tube. When air bubbles cease to be disengaged, the suction is interrupted and the stopper withdrawn. Water is now run in from the burette till the flask is filled to the mark, care being taken to work down any coal which may have stuck to the neck.

The results may be calculated as follows:

$$\text{Specific Gravity} = \frac{100}{V_0 - V_1}$$

wherein V_0 = volume of the flask; V_1 = number of cc. water added to coal.

No calculation at all need be made if a table of reciprocals be available, as specific gravity = 100 × reciprocal of $V_0 - V_1$. As an example 100 grams coal were taken; volume of flask, $V_0 = 262$ cc.; volume of water added to coal, $V_1 = 197$ cc.

$$\text{Specific Gravity} = \frac{100}{262 - 197} = 100 \times \frac{1}{65} = 1.54.$$

After making a determination the flask is emptied and rinsed, then allowed to drain for one minute, when another determination may be made.

This method is very rapid and so simple that an inexperienced operator can without difficulty make over 80 determinations per day accurate to within 0.02 unit of specific gravity. It is, of course, self-evident that this method has a wide range of applicability; the gravities of such materials as rocks, drillings, etc., may be determined with ease.

While the authors claim nothing new or radical in this process, still they submit it as a procedure by which results of moderate accuracy can be obtained with great rapidity, while the outlay for special apparatus is practically nil.

ABRAHAM G. BLAKELEY.
EDWIN M. CHANCE.

LABORATORY OF THE
P. & R. COAL & IRON CO.,
POTTSVILLE, PA.

LIQUID MIXTURES FOR MAXIMUM AND MINIMUM THERMOMETERS.

A homogeneous liquid mixture may, by a change of temperature or by certain additions, become separated into two layers. For example, a mixture of 15 cc. amyl alcohol, 20 cc. ethyl alcohol, and 32.9 cc. water is homogeneous above 20° C.; but the least lowering of temperature below this, even by one-tenth of one degree, causes the division of the liquid into two nearly equal layers. This phenomenon can be made use of in the construction of an exceedingly delicate minimum thermometer. Convenient volumes of amyl and ethyl alcohols are mixed together, brought to the required temperature, and water gradually added, drop by drop, until a slight turbidity results. The liquid is then sealed in a tube, being first colored with carmine whenever the temperature falls below that at which it was prepared, the two layers separate, and are of different shades. If methyl and ethyl alcohols be used in the same way a maximum thermometer can be prepared.

ROBT. E. BRADLEY.

THE RAPID DETERMINATION OF MANGANESE IN STEEL.

All methods whether color or volumetric, dependent on the oxidation to permanganic acid by red lead or lead dioxide, suffer from the disadvantage of organic matter in these reagents which reduces the Mn_2O_7 after it is formed. Still it is possible to get red lead that serves the purpose, provided a sharp look-out is kept for splints of wood in the liquid after the boiling, and the test is repeated, or done in duplicate with a fresh portion of the standard. But in addition there is a source of error from the carbon in certain steels. It seems that in certain steels—but these steels are the exception and not the rule—the carbon is in such a condition that red lead (or lead dioxide) does not completely oxidize it, and therefore what is left of the carbon after the boiling with this reagent reduces the permanganic acid to a certain extent, so that repeated results, although agreeing with each other, are too low. The obvious remedy for this is to get rid of the carbon first. The writer therefore finds it convenient to use the filtrate from the silicon determination for the manganese determination, as follows: 2.3510 grams steel are dissolved in 50 cc. water and 10 cc. strong sulphuric acid and evaporated to dense fumes. Then boiled up with water and filtered into an Erlenmeyer flask marked at 200 cc., and the silica washed twice with water. The filtrate is then diluted to the mark, mixed, 25 cc. withdrawn with a pipette, and transferred to a tall narrow 100 cc. beaker marked at 50 cc. Then diluted up to this mark roughly with 1.20 nitric acid, boiled 15 minutes, removed from the heat and the red lead at once added and stirred, then diluted carefully to the mark, and stirred again. The lead sulphate formed settles instantly and carries with it the excess lead oxide, so that the comparison of the color with a standard steel which has gone through the same process can be made at once (and the quicker the better) by withdrawing 5 cc. with a pipette and transferring to ordinary color carbon comparison tubes. The following results on basic open-hearth steels illustrate this source of error.

	Per cent.
No. 15072 by Williams' method (at another works)......	about 0.39
No. 15072 by ordinary color method..................	0.315–0.345
No. 15072 by modified color as above................	0.39
No. 15072 by Volhard's method......................	0.39
No. 15082 by Williams' method (at another works)......	about 0.57
No. 15082 by ordinary color method......	0.435–0.455–0.415–0.435
No. 15082 by modified color as above................	0.555
No. 15082 by Volhard's method......................	0.57

The color tests by Mr. A. Kabline.

GEORGE AUCHY.

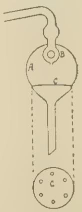
A MODIFIED KJELDAHL CONNECTING BULB.

EDITOR OF THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY:

DEAR SIR: In your October issue, page 737, there was described a modified Kjeldahl Connecting Bulb; the modification will be useful.

I would, however, call attention to another modified form which I designed and have had in use for some time in my laboratory, and is now being used by many other chemists in England.

It consists of a large bulb A, somewhat pear-shaped about 7 cm. in diameter, inside which, to the outlet from the large bulb, is attached a smaller bulb, B, about 2 cm. in diameter with a hole about 8 mm. diameter blown in the side and an opening about 2 mm. diameter at the bottom. At the lower part of the large bulb is fixed a thin glass plate C perforated with about six holes; the holes are towards the sides of the plate as far as possible from the centre.



This form of bulb has a wide application and especially in the estimation of volatile fatty acids in butter and butter substitutes, ammonia, arsenic and antimony by the distillation method, for the distillation of tar and tar oils and gen-

erally where the liquid is liable to bump or froth up during the boiling. The risk of spray being carried over into the distillate is practically nil.

Messrs. J. W. Towers & Co., Ltd., Widnes, England, now make and keep a stock of these bulbs.

Yours faithfully,

G. Watson Gray.

Liverpool, October 22, 1909.

BOOK REVIEWS AND NOTICES.

Reinforced Concrete in Europe. By Albert Ladd Colby. Cloth, 8vo. 260 pp. Easton, Pa.: Chemical Publishing Co.

Mr. Colby has given us in the present volume the results of his extended travel and research abroad in the investigation of the status of reinforced concrete in the principal European countries, its applications, cost and economy, endurance and resistance to fire and other destructive agents, the various systems in use and details of construction. It is a reference work, solely, and presents in convenient form information and data, much of which would otherwise be inaccessible to American engineers. The work shows great care in preparation and arrangement; it is concise but comprehensive and represents a vast amount of work in investigation and painstaking sifting and arrangement of data. It includes authoritative opinions, government rules, recommendations and specifications of cement for reinforced concrete, the metal used for reinforcement, and the mechanbond and form of bars. It covers the practice in England, France, Germany, Austria, Hungary, Switzerland and Italy. It also contains lists and description of foreign government and private testing stations, congresses, technical institutions, associations and committees who have endorsed reinforced concrete as a material of construction or who have adopted resolutions, specifications or rules relating thereto. There is, also, a complete bibliography of books, journals, proceedings, etc., published at home and abroad, giving the date of publication and price of each. Addresses of prominent engineers in each country and of the official and technical testing stations and the various committees and associations add to the value of the volume. As stated, it is essentially a reference work and should be in every working and reference engineering library.

Ernest B. McCready.

Laboratory Notes on Iron and Steel Analyses. By Walter MacFarlane. Cloth-bound, pages xvi and 462, 5 × 7½ in. 25 illustrations, published by Longmans, Green & Co. New York and London. Price, $2.50 net.

This volume is the third book by the author on subjects relative to iron and steel, his previous publications being "Laboratory Notes on Practical Metallurgy" and "The Principles and Practice of Iron and Steel Manufacture."

The present volume is a detailed description of actual analytical methods used in daily practice in an iron and steel laboratory in England, which was under the supervision of the author for a number of years. The aim of the book, as stated by the author, has been to set out the complete course of an assay or an analysis in full detail, specifying precise quantities of reagents and convenient sizes of apparatus to be used.

The methods given cover the analysis of all raw materials, products, and by-products, special steels, and many miscellaneous estimations that are necessary to the manufacture of iron and steel.

Fifty-five pages are devoted to "Notes on Sampling," "General Notes on Laboratory Operations and Appliances," "Notes on Preparing and Storing Solutions."

A supplement contains the methods for "Analysis of Iron Ores" as published by the Chemical Committee of the United States Steel Corporation.

The methods given, with a few exceptions, are those in general use in the iron and steel laboratories of the United States. Examples and calculations are numerous and will prove valuable aids to students and to those to whom the work is new.

As stated the author's aim is to give detail, and like a good sportsman his aim has been true. The demand for such a publication is growing.

The print, paper and binding of the book are excellent.

William Brady.

Alloys and Their Industrial Application. By Edward F. Law. pp. 7 + 270. Numerous plates. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott. 1909. Price, $4.00 net.

This is an excellent and comprehensive treatise on alloys, systematically considered. After a general introduction, the properties of alloys are considered and the methods of investigation. In the chapter on constitution the application of the phase rule is taken up and also the graphic representation of the properties of alloys. One chapter is devoted to the influence of temperature on the properties of alloys and another chapter to the corrosion of alloys. Three chapters are devoted to copper alloys, one to nickel-copper and special copper alloys, one to lead, tin and antimony alloys, one to anti-friction alloys, one to aluminum alloys, and one to silver and gold alloys. The iron alloys are treated in a chapter of thirty-one pages, which may seem to some too brief a space for this important subject. However, it may be said that the book in general is well proportioned.

Tanners and Chemists Handbook. By Lewis E. Levi and Earl V. Manuel. pp. 363. 8vo. Milwaukee, Wis. Published by the authors. Price, $5.00.

The authors are chemists with the Pfister & Vogel Leather Company, and undertake in this work to give various tables and other data and methods of analysis of interest to tanners' chemists. It is a useful book but contains a good many tables of easy access elsewhere, for instance in the *Chemiker Kalender*, in smaller and more convenient form. The book is marred by the insertion of advertisements at various points in the body of the book. There is a dictionary of tanning terms, giving English and German equivalents. The price may seem to some rather higher than it should be.

Chemical Conversion Tables for Use in the Analysis of Commercial Fertilizers, Cottonseed, Iron and Food Products. By H. B. Battle and W. J. Gascoyne. pp. 79. 12mo. Baltimore: Williams & Wilkins Pub. Co. 1909. Price, $2.50.

This work contains tables for various conversions used in the analytical laboratory, and is without question a useful

work for the busy routine analyst. It has an indented index for ready reference. It will undoubtedly prove of value in the works, commercial and control laboratory where many calculations have to be made quickly. The tables are based on the International Atomic Weights of 1909, as reported by the International Committee. While somewhat high, the price cannot be considered exorbitant for the man who needs such a work, considering the amount of labor required in its preparation and the limited sale for such a book.

Transactions of the American Institute of Chemical Engineers. Vol. I. 1908. pp. 202. Charts and plans in pocket. Large 8vo. New York: D. Van Nostrand Co. Price, $6.00 net.

This, the first volume of *Transactions of the American Institute of Chemical Engineers*, contains the preliminary discussion and committee reports leading up to the formation of the Institute and some ten scientific papers with discussions presented to the Institute. There is a list which shows that there were one hundred and one members in June, 1909. The papers, considered as a whole, are good and useful to the chemical engineer.

Practical Points for Practical Brewers. By FRANCIS WYATT and EMIL SCHLICHTING. Small 12mo. pp. 176. New York: National Brewers Academy.

This is a small volume of tables, data and calculations of interest to brewers.

Prevention of Industrial Accidents. No. 1. General Pamphlet. By FRANK E. LAW and WM. NEWELL. 12mo. pp. 195. New York: Fidelity & Casualty Co. Price, 25 cents.

This timely and really valuable pamphlet should be in the hands of all works engineers and superintendents. It contains much valuable data relating to accidents in manufacturing plants and around machinery and the prevention thereof. Incidentally, many valuable points are noted relating to the handling of steam boilers, engines, elevators and the factory in general.

Briquetting Tests, at the United States Fuel-Testing Plant, Norfolk, Va., 1907–1908. By CHAS. L. WRIGHT. *Bull.* **385,** *U. S. Geological Survey.* 8vo., pp. 41. Washington: Government Printing Office. 1909.

This bulletin is of value to coal dealers and fuel engineers and gives in some detail the machinery, and the methods used in briquetting and the tests of briquetting made in various ways from different kinds of coal. At the end of the descriptive matter there is a good bibliography on fuel testing and briquetting.

The United States Geological Survey has just issued a bulletin on "Commercial Deductions from Comparisons of Gasoline and Alcohol Tests on Internal-Combustion Engines," by Robert M. Strong. The tests, which were under the technical direction of R. H. Fernald, engineer in charge of the producer-gas section of the technologic branch, were conducted at the fuel testing plant in St. Louis, Mo., and at Norfolk, Va. The tests dealt primarily with gasoline, forming part of the investigation of mineral fuels provided for by acts of Congress. To determine the relative economy and efficiency of gasoline it was compared with denatured alcohol. When the series of tests was started, it was found that it took from one and one-half to two times as much alcohol as gasoline to produce a given power. With special alcohol engines, entirely suited to the use of alcohol, the latter fuel has been made to do as much work, gallon for gallon as the gasoline.

The Fuel Supply Committee of the Boston Chamber of Commerce has just issued a report on "The Buying and Handling of Steam Coal." In this report a table is given, which shows the average of over 2,000 analyses of coal, tabulated according to various districts in Pennsylvania, Maryland, West Virginia, and Virginia. These analyses have been compiled from bulletins of the U. S. Geological Survey, as well as various commercial interests who are analyzing their coal or having it analyzed. The latter comprises over 1,700 analyses and referring to this the report states: "In compiling these analyses, care and discretion were used in order that only those analyses made from representative samples by proficient chemists should be included. A special representative was engaged to investigate the methods of sampling and analysis, and compile the data of the many consumers who are analyzing the coal which they receive. Many instances were encountered where the results were obviously inaccurate and unreliable, and they were consequently not included in the results presented herewith." In addition to showing the average of the Government and commercial analyses separately in the different districts, they also show the variation in the different constituents of the coal as shown by analysis and B. t. u. This enables one to not only determine the approximate average quality of coal from any one district, but also indicates the variations which may be expected in the moisture, volatile, fixed carbon, ash, sulphur, and B. t. u. independently. There are in all twenty districts represented. There is also given a diagram, showing graphically the variation in each of these constituents from the nine districts from which New England receives the greater part of its coal supply. This diagram is very interesting in that it shows the greater variation in quality of some districts than in others. This report gives more comprehensive and reliable data concerning the quality of coal as shipped from the Northern Appalachian coal fields than has heretofore been published. In this respect it is not only of interest to the chemists and coal consumers of New England but to all those who receive or analyze coals from this part of the country. A few analyses of Rhode Island and Nova Scotia coal are also included.

Statistics have been compiled which show the annual coal consumption of the New England states to be over 24,000,000 tons. The report also indicates the quantity of this coal as received by all rail and tide water at the various discharging ports, distinguishing between anthracite and bituminous.

Considerable other data and information are given concerning the transportation and handling of coal. Accompanying this report are three maps, one showing the location of the various districts in the Northern Appalachian coal field. The other two are maps of New England, one giving freight rates from the different mining districts to the various stations throughout New England, while the other gives the rates on coal shipped from tide water discharging ports. These maps are 44″ × 60″, and are lithographed, showing each 25 cents change in rate in a different color. The smaller changes are indicated by figures. These maps are very

interesting in showing the effect of competition upon rate-making and enable a person to determine the freight rate on coal from any mining district to any point in New England by either all rail or tide water shipment. A copy of this report, including maps, may be obtained from the secretary of the Fuel Supply Committee of the Boston Chamber of Commerce, Boston, Mass., for $2.50. E. G. BAILEY.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, PHILADELPHIA MEETING.

WEDNESDAY, DECEMBER 8, 1909.

10.00 A.M.
Meeting at Hotel Walton.
Address of Welcome. Mayor John E. Reyburn.
Business Session.
Reports of Officers and Council.
Reports of Committees.

11.30 A.M.
Reading of Papers.
(1) "Natural Draft Gas Producers and Gas Furnaces," by Ernest Schmatolla. Discussion by O. K. Zwingenberger and G. E. Barton.
(2) "The Commercial Extraction of Grease and Oils," by Wm. M. Booth. Discussion by Frederick Dannerth, Louis Olney and Samuel P. Sadtler

12.30 P.M.
Luncheon at Hotél Walton (75 cents Table d'Hote).

1.30 P.M.
Visit to Chemical, Engineering and Physical Laboratories of the University of Pa.
Visit to Commercial Museum of Philadelphia. Dr. W. P. Wilson.

1.00 P.M.
Luncheon at Works of Harrison Bros. & Co., Gray's Ferry Road.
Excursion through works (admission by card only).

7.30 P.M.
Address by Retiring President.
Address—"The Chemical Industries of America," by Prof. Chas. E. Munroe.

THURSDAY, DECEMBER 9TH.

9.30 A.M.
Members of the Institute and their guests will assemble at Race St. wharf on the Delaware and be conveyed by the city boat *S. H. Ashbridge* to the Torresdale Filtration Plant—returning stop at Tacony to visit the Wool Degreasing Plant of Erbin, Harding & Co.

12.30 P.M.
Luncheon at the works of the Welsbach Light Co. as the guests of the Company.

1.30 P.M.
Excursion through the works of the Welsbach Light Co.

3.00 P.M.
Return by boat to Kaighn's Point and excursion through By-Product Coke Oven Plant of the Camden Coke Co.

5.00 P.M.
Return to Chestnut St. wharf, Philadelphia.

7.00 P.M.
Subscription Dinner at Hotel Walton, $3.00.

FRIDAY, DECEMBER 10TH.

9.30 A.M.
Installation of Officers and Business Meeting.

10.30 A.M.
Reading of Papers.
(3) "Multiple Effect Distillation," by F. J. Wood (Mechanical Engineer of Marx & Ravolle's Glycerine Refinery).
(4) "The Advantages of the Multiple Effect Distillation of Glycerine and Other Products," by A. C. Langmuir. Discussion by S. S. Sadtler and Chas. L. Reese.
(5) "Reclaiming of Waste India Rubber," by S. P. Sharples. Discussion by Wm. M. Grosvenor.

12.00 M.
Luncheon at Hotel Walton.

1.00 P.M.
Leave Broad St. Station for Trenton, N. J.

2.00 P.M.
Excursions—Trenton Potteries.
The Hamilton Rubber Co.
Linoleum Works.

7.30 P.M.
Reading of Papers.
(6) "Materials for Textile Chemical Machines," by Frederick Dannerth. Discussion by Louis A. Olney and J. M. Matthews.
(7) "The Manufacture of Carbon Bisulphide," by Edward R. Taylor.
(8) "Chemical Composition of Illinois Coal," by A. Bement.
(9) "Heat Efficiency of Smokeless Combustion, and Heat Absorbing Capacity of Boilers," by A. Bement.

9.00 P.M.
Final Business Meeting.

SATURDAY, DECEMBER 11TH.

Visit to Cement Plant at Allentown, Pa.
Headquarters at Hotel Walton.

AMERICAN SOCIETY FOR TESTING MATERIALS.

COMMITTEE ON STANDARDIZED SPECIFICATIONS FOR COAL.

On June 28 and 29, 1909, there were several meetings of the Committee on Standard Specifications for Coal of the American Society for Testing Materials at the Hotel Traymore, Atlantic City, New Jersey. As a result of these meetings, and the work accomplished through correspondence since the organization of this committee on January 29th, the following preliminary report was submitted by J. A. Holmes, chairman, and was later approved by a majority of the members of this committee. The complete membership of the various sub-committees of this committee was given in the June number of THIS JOURNAL.

In carrying out the instructions of the Society, its Executive Committee has authorized and approved a committee of sixty-seven members to consider and report on the subject of specifications for the purchase of coal.

The first meeting of this committee was held at the Fort Pitt Hotel, Pittsburg, Pa., January 29, 1909. The committee was there organized by the selection of J. A. Holmes as Chairman, B. F. Bush as Secretary, and with sub-com-

mittees to take up the consideration of specifications as applied to the following classes of coals:

- Sub-Committee No. 1, on Coals for Steam Power Plants, W. F. M. Goss, Chairman.
- Sub-Committee No. 2, on Coals for Producer Gas Plants, R. H. Fernald, Chairman.
- Sub-Committee No. 3, on Coals for Domestic and Heating Plants, J. E. Woodwell, Chairman.
- Sub-Committee No. 4, on Metallurgical Coals, C. F. Robinson, Chairman.
- Sub-Committee No. 5, on Coals for Illuminating Gas, Alfred H. White, Chairman.
- Sub-Committee No. 6, on Coals for Cement Drying, Brick Kilns, etc., Edward Orton, Jr., Chairman.
- Sub-Committee No. 7, on Sampling and Testing of Coals, D. T. Randall, Chairman.
- Sub-Committee No. 8, on Forms of Contract in Coal Purchases, E. H. Taylor, Chairman.
- Sub-Committee No. 9, on Educational Work in behalf of more Efficient Mining, Preparation, and Use of Coal, J. A. Holmes, Chairman.

The practicability of adopting specifications for the purchase of the above different classes of coals has been discussed by correspondence among the members of the several sub-committees named above, and the general subject of coal specifications has been discussed individually, by correspondence and occasional personal interviews between members of the committee, during the past several months. No forms of specifications have as yet been agreed upon, however, and your committee at this time can but submit a preliminary statement as a report of progress, and ask to be continued.

The committee recognizes the growing interest in the general subject of the purchase of materials under specifications, and it is believed that in all cases where a rational basis for such specifications can be agreed upon, the results of such practice must be beneficial to both producer and consumer, as it enables the consumer to point out more specifically just what he wants; it enables the producer to offer bids on a more intelligent basis, and it makes easier equitable settlements.

In any industry, however, the sudden introduction of a system of ill-digested specifications is likely to work hardship, especially on the producer, without compensating benefits even to the consumer. This is especially apt to be true in an industry so large, so little organized, and contending with so many unsettled problems, as the soft coal industry of to-day. Some of the recently promulgated specifications for the purchase of coal show the extremes to which this system may be carried before the difficulties involved are adequately understood.

Thus one of these recent specifications prescribes that the coals offered for use at a station within easy reach of one of the coal fields should have 15,000 British thermal units and not exceeding 3.25 per cent. ash, 1.00 per cent. sulphur, and 0.90 per cent. moisture. Other specifications have been recently adopted in a number of cases which are equally impracticable and unnecessarily stringent, which prescribe no satisfactory methods of sampling or testing the coals, render premiums impossible and penalties inevitable on coals, the prices of which are already so low as to leave no possibility of profit to the producer except by involving extensive and permanent waste of coal in mining. Still other specifications have been fully as irrational and unfair, because leaving the sampling and testing, and in fact the adjustment of differences, entirely in the hands of one of the interested parties, and based on inadequate tests.

Your committee desires to emphasize at this time certain reforms which are regarded as fundamental accompaniments or outgrowths of the present movement for specifications, and which are essential to the welfare of the coal industry in the United States, namely:

(1) A classification of coals with respect to fuel efficiency; the adaptation of equipment to coals for obtaining the greatest efficiency from each class of these fuels; the continued use at each plant of that type of fuel best adapted to the equipment; the use of low-grade fuels either at the mines or within short distances, and of the high-grade fuels under conditions demanding highest efficiency and requiring distant transportation.

(2) Special efforts on the part of architects and engineers to provide everywhere adequate space for power and heating plants and proper equipment, with a view to making the most efficient use of the fuels that are most available.

(3) Such readjustment in the prices at the mines of the different classes of coals as will render possible clean and safe mining, and the use at local or distant points of all grades of coal worthy of being placed on the fuel list.

The realization of these essential reforms will naturally be slow of accomplishment, but for the hastening of this accomplishment every engineer, and indeed every citizen of the country, should, as a national duty, contribute to the best of his ability.

The committee deprecates the hasty adoption of extreme specifications such as those mentioned above, for the reason that such action does not help but hinders this movement, without any compensating benefits to either producer or consumer. At the same time the committee recognizes the fact that a proper specification should and will, when understood, encourage the use of all grades of fuels; and it should provide, as do some of those now in force, an equitable basis for the adjustment of the differences between producers and consumers.

If continued, your committee will endeavor to submit for the later consideration of the Society forms of specifications for the several types of coal mentioned above, in so far as the use of such specifications may be considered as helpful to industry, and contributing to the equitable relations between interested parties.

Respectfully submitted on behalf of the committee,

J. A. Holmes, *Chairman*,
B. F. Bush, *Secretary*.

AMERICAN CHEMICAL SOCIETY, BOSTON MEETING.

The Boston meeting of the American Chemical Society, held during convocation week, in conjunction with the American Association for the Advancement of Science, will be reported in the February number of This Journal. In particular, the meetings of those Divisions devoted to applied chemistry will be reported in as much detail as possible. These Divisions include the Division of Industrial Chemists and Chemical Engineers; the Division of Agricultural Chemists; the Division of Pharmaceutical Chemists; and the Division of Agricultural and Food Chemists.

OFFICIAL REGULATIONS AND RULINGS.

(T. D. 29957.) *Denaturing of Olive Oil under Paragraph 639 of the Tariff Act of August 5, 1909.*

TREASURY DEPARTMENT, August 20, 1909.

To Collectors and Other Officers of the Customs:

Paragraph 639 of the Tariff Act of August 5, 1909, provides for the free entry of:

Olive oil rendered unfit for use as food or for any but mechanical or manufacturing purposes, by such means as shall be satisfactory to the Secretary of the Treasury and under regulations to be prescribed by him.

Olive oil to be entitled to entry under the foregoing provision of law either must have been denatured abroad in such a manner as to satisfy the collector that it is permanently unfit for use as food or for any but mechanical or manufacturing purposes, or it must be denatured after arrival, under customs supervision and at the expense of the importer, by one of the following methods, to be elected by the importer:

To 100 gallons of the olive oil to be denatured add any of the following substances:

(*a*) 3 gallons rosin oil, preferably second or third runs.

(*b*) 3 gallons refined destructively distilled wood turpentine, boiling not lower than 160° C.

(*c*) 3 gallons mineral oil such as spindle oil, or a rather crude kerosene.

(*d*) 1/4 gallon pyridin.

(*e*) 1/2 gallon creosote.

(*f*) 3 gallons aniline oil.

(*g*) 6 gallons dark-colored oleic acid.

Oil denatured according to formulae *b*, *d*, *e* and *f* must be marked as poisonous.

The officer supervising the denaturing is enjoined to take particular care to have the denaturant thoroughly incorporated with the olive oil.

"Sulphured olive oil" obtained by the extraction of olive oil from press cake by means of carbon bisulphid need not be further denatured.

The Department will from time to time prescribe additional formulae, and will consider any formula for special denaturation that may be submitted by any manufacturer.

To insure the protection of the revenue, 100 per cent. of all olive oils claimed to be inedible, or to have been denatured abroad, will be sampled.

No olive oil will be released free of duty under the said paragraph of law until the owner or consignee shall have filed with the collector of customs an affidavit in the following form:

PORT OF ————.

I, ————, do solemnly declare that I am the owner or consignee of the olive oil described in the invoice and entry hereto attached, that the same is permanently unfit for use as food and is specially imported in good faith for mechanical or manufacturing purposes.

———— ————.

(Owner or consignee.)

Subscribed and sworn to before me this —— day of ————, 19——.

———— ————.

(Title of officer.)

JAMES B. REYNOLDS, *Acting Secretary.*

(T. D. 1529.) *Denatured Alcohol.*—Formula 1 authorized for use in the manufacture of acetaldehyde.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
WASHINGTON, D. C., August 10, 1909.

SIR: The application has been received and considered by this office of ———— for permission to manufacture acetaldehyde from denatured alcohol under the provisions of Section 40, Part VI of Regulations 30, and for the authorization of formula 1 as a special denaturant for use in its manufacture.

You are informed that the desired permission is hereby accorded provided the acetaldehyde contains no undecomposed alcohol. * * *

Respectfully,
J. C. WHEELER,
Acting Commissioner.

MR. FRANK MCCORD,
Collector Eighteenth District, Cleveland, Ohio.

(T. D. 1539.) *Adulterated Butter.*

Officers are instructed to secure more than one sample from unbroken original packages, if possible, before recommending assessment, and that samples from partly emptied or retail packages should be forwarded only as corroborative evidence.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
WASHINGTON, D. C., September 14, 1909.

To Collectors, Internal Revenue Agents, and Others:

Attention is called to the necessity of securing, if possible, samples from more than one unbroken original package of butter for analysis, where such samples alone are to be made the basis of assessment of special tax as manufacturer of adulterated butter and stamp tax on product found to contain 16 per cent. or more of moisture.

Officers should not forward samples from partly emptied original packages or retail packages which might have a pronounced moisture content owing to the possible precipitation of water from the portion removed into the butter remaining in the tub or other receptacle, except as corroborative evidence of other samples taken from unbroken original packages.

Great care should be exercised in securing and identifying the samples as the product of the specific manufacturer against whom assessment is recommended, as this evidence might be the basis of action in court.

No assessment should be so recommended upon the basis of a single sample taken from a broken package, or even a single original package intact, unless there is other evidence tending to establish liability to tax.

Nothing in this decision is to be construed as in conflict or in any way modifying T. D. 1449 and T. D. 1498 upon this subject.

ROYAL E. CABELL,
Commissioner.

The following Notice of Judgments has been issued by the Board of Food and Drug Inspection on November 11 and 16, 1909.

102. Misbranding of distiller's dried grains (as to protein and fat content).

103. Adulteration of eggs (presence of putrid and decomposed animal matter).

104. Adulteration and misbranding of stock feed (as to presence of rice hulls).

105. Adulteration and misbranding of a cereal (as to presence of wheat)

106. Misbranding of a cane sirup (as to presence of glucose).

107. Misbranding of Vermont or maple sugar (as to presence of cane sugar).

108. Misbranding of preserves (underweight).

109. Adulteration and misbranding of cottonseed meal (as to presence of cottonseed hulls).

110. Misbranding of sirup (as to quantity).

111. Misbranding of catsup (as to amount of benzoate of soda present).

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